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⑭合成樹脂組成物

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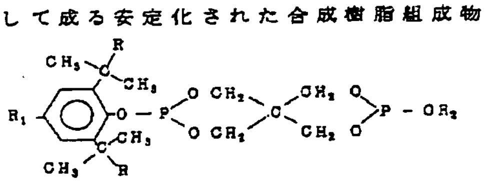
明　細　書

1. 発明の名称

合成樹脂組成物

2. 特許請求の範囲

合成樹脂にフエノール系抗酸化剤及び次の一般式(I)で示される有機ホスファイト化合物を添加して成る安定化された合成樹脂組成物。


(I)

（式中Rは炭素原子数1～6のアルキル基を示し、R_1はメチルまたはエチル基を示し、R_2はアルキルまたはアリール基を示す）

3. 発明の詳細な説明

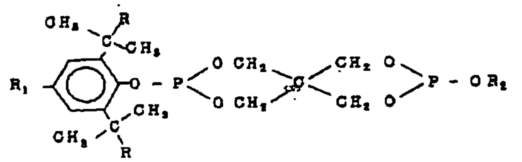
本願発明は合成樹脂組成物に関し、詳しくはフエノール系抗酸化剤及び特定のホスファイト化合物を添加することによつて、熱及び光の作用による劣化に対して長期にわたつて安定化された合成樹脂組成物に関する。

ポリエチレン、ポリプロピレン、ポリスチレン、ポリ塩化ビニル等の合成樹脂は熱及び光の作用により劣化し、着色したり、機械的強度が低下し使用に耐えなくなることが知られている。かかる合成樹脂の劣化を防ぐ為にこれまで多くの添加剤が単独であるいは種々組み合わせて用いられてきた。これらの添加剤の中でもホスファイト系の化合物は合成樹脂に対して耐熱性、耐光性を付与し、しかも合成樹脂の着色を抑制するという利点があり広く用いられてきた。これらのホスファイト化合物の中でも、トリス(ノニルフエニル)ホスファイト、ジフエニルイソデシルホスファイト、ジステアリルペンタエリスリトールジホスファイト、テトラアルキルビスフエノールAジホスファイト等は比較的その効果が大きく、合成樹脂用安定剤として賞用されていた。

しかしながら、従来用いられていたホスファイト化合物はその効果が比較的短時間で失なわれることが多く、特に屋外あるいは湿潤雰囲気

で使用するとその効果が急速に失なわれることが多かつた。また、従来用いられてきたホスファイト化合物の高温での安定化効果は一時的なものにすぎず、長期的な安定化効果は小さく実用上まだまだ不満足なものであつた。

本発明者等はかかる現状に鑑み鋭意検討を重ねた結果フエノール系抗酸化剤と次の一般式(I)で示される有機ホスファイト化合物の併用が長期的な安定化効果が大きくしかも屋外あるいは湿潤雰囲気での使用時にも効果が低下しないことを見い出し本発明に到達した。


(I)

(式中、Rは炭素原子数1～6のアルキル基を示し、R_1はメチルまたはエチル基を示し、R_2はアルキルまたはアリール基を示す)

以下にフエノール系抗酸化剤及び一般式(I)で示される有機ホスファイト化合物について詳述する。

本発明に使用されるフエノール系抗酸化剤としてはたとえば、2,6－ジ－第3ブチル－p－クレゾール、2,2′－メチレンビス(4－メチル－6－第3ブチルフエノール)、4,4′－メチレンビス(2,6－ジ－第3ブチルフエノール)、2,2′－メチレンビス〔6－(1－メチルシクロヘキシル)p－クレゾール〕、2,2′－メチレンビス(4－エチル－6－第3ブチルフエノール)、2,2′－メチレンビス(4－メチル－6－ノニルフエノール)、4,4′－イソプロピリデンビス(2,6－ジ－第3ブチルフエノール)、4,4′－ブチリデンビス(2,6－ジ－第3ブチルフエノール)、4,4′－ブチリデンビス(6－第3ブチル－m－クレゾール)、1,1,3－トリス(2－メチル－4－ヒドロキシ－5－第3ブチルフエニル)ブタン、2,6－ビス(2－ヒドロキシ－3－ノニル－5－メチルベンジル)－4－メチルフエノール、チオジグリコールビス(3,5－ジ－t－ブチルフエニル－4－ヒドロキシフエニルプロピオネート)、ステアリル－β－(4－ヒドロキシ－3,5－ジ－第3ブチルフエニル)プロピオネート、1,3,5－トリス〔(3,5－ジ－第3ブチル－4－ヒドロキシフエニル)プロピオニルオキシエチル〕イソシアヌレート、ビス(4－第3ブチル－3－ヒドロキシ－2,6－ジメチルベンジル)ジチオールテレフタレート、テトラキス〔メチレン－3－(3,5－ジ－第3ブチル－4－ヒドロキシフエニル)プロピオネート〕メタン、1,3,5－トリス(3,5－ジ－第3ブチル－4－ヒドロキシベンジル)－2,4,6－トリメチルベンゼン、ジステアリル(4－ヒドロキシ－3－メチル－5－第3ブチル)ベンジルマロネート、1,3,5－トリス(3,5－ジ－第3ブチル－4－ヒドロキシベンジル)イソシアヌレート、ステアリル(3,5－ジ－メチル－4－ヒドロキシベンジル)チオグリコーレート、ビス〔3,3－ビス(4－ヒドロキシ－3－第3ブチルフエニル)ブチリックアシド〕グリコールエステル、2－オクチルチオ－4,6－ジ(4－ヒドロキシ－3,5－ジ－第3ブチル)フエノキシ－1,3,5－トリアジン、4,4′－チオビス(6－第3ブチル－m－クレゾール)、1,3,5－トリス(2,6－ジ－メチル－3－ヒドロキシ－4－第3ブチルベンジル)イソシアヌレートなどがあげられヒドロキシフエニルプロピオン酸エステル化合物及びイソシアヌレート環を有する化合物が好ましい。

フエノール系抗酸化剤の添加量は樹脂100重量部に対して、0.001～5重量部である。

一般式(I)において、Rで示される炭素数1～6のアルキル基としてはメチル、エチル、プロピル、イソプロピル、ブチル、イソブチル、2,2－ジメチルプロピル、ペンチル、ヘキシル等の基があげられる。

R_2で示されるアルキル基としてはメチル、エチル、プロピル、イソプロピル、ブチル、第2ブチル、第3ブチル、アミル、第3アミル、イソアミル、ヘキシル、イソヘキシル、ヘプチル、

オクチル、イソオクチル、2－エチルヘキシル、デシル、イソデシル、ラウリル、オレイル、トリデシル、$C_{12\sim15}$混合アルキル、ステアリル等の基、更にシクロペンチル、シクロヘキシル、シクロオクチル、シクロドデシル、4－メチルシクロヘキシル等のシクロアルキル基、ベンジル、2－フエニルエチル、3－フエニルプロピル、2－フエニルプロピル等のアリールアルキル基、フルフリル、テトラヒドロフルフリル、5－メチルフルフリル及びα－メチルフルフリル基、又はメチル－、エチル－、イソプロピル－、ブチル－、イソブチル－、ヘキシル－、シクロヘキシル－、フエニルセロソルブ残基；メチル－、エチル－、イソプロピル－、ブチル－、イソブチルカルビトール残基；トリエチレングリコールモノメチルエーテル、－モノエチルエーテル、－モノブチルエーテル残基；グリセリン－1,2－ジメチルエーテル、－1,3－ジメチルエーテル、－1,3－ジエチルエーテル、－1－エチル－2－プロピルエーテル残基；ノニルフエノキシポリエトキシエチル、ラウロキシポリエトキシエチル等のエーテル結合を有するアルキル基があげられる。

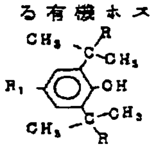
R_2で示されるアリール基の例としてはフエニル、フエニルフエニル、ナフチル等の基、更にトリル、キシリル、エチルフエニル、ブチルフエニル、第3ブチルフエニル、オクチルフエニル、2,6－ジ－第3ブチル－4－メチルフエニル、2,6－ジ－第3ブチル－4－メトキシカルボニルエチルフエニル、イソオクチルフエニル、第3オクチルフエニル、ノニルフエニル、2,4－第3ブチルフエニル等のアルキルアリール基、シクロヘキシルフエニル、シクロオクチルフエニル等のシクロアルキルアリール基、4－メトキシフエニル、4－エトキシフエニル、3－ラウロキシフエニル、2－メトキシ－4－メチルフエニル、2－t－ブチル－4－メトキシフエニル、4－ベンジルオキシフエニル、3,4－メチレンジオキシフエニル等の基があげられる。

従つて、一般式(I)で示される代表的なホスファイト化合物としては、2,6－ジ－t－ブチル－4－メチルフエニル・フエニル・ペンタエリスリトールジホスファイト、2,6－ジ－t－ブチル－4－メチルフエニル・メチル・ペンタエリスリトールジホスファイト、2,6－ジ－t－ブチル－4－メチルフエニル・2－エチルヘキシル・ペンタエリスリトールジホスファイト、2,6－ジ－t－ブチル－4－メチルフエニル・イソデシル・ペンタエリスリトールジホスファイト、2,6－ジ－t－ブチル－4－エチルフエニル・ラウリル・ペンタエリスリトールジホスファイト、2,6－ジ－t－ブチル－4－エチルフエニル・イソトリデシル・ペンタエリスリトールジホスファイト、2,6－ジ－t－ブチル－4－メチルフエニル・ステアリル・ペンタエリスリトールジホスファイト、2,6－ジ－t－ブチル－4－メチルフエニル・シクロヘキシルペンタエリスリトールジホスファイト、2,6－ジ－t－ブチル－4－エチルフエニル・ベンジル・ペンタエリスリトールジホスファイト、2,6－ジ－t－ブチル－4－メチルフエニル・エチルセロソルブ・ペンタエリスリトールジホスファイト、2,6－ジ－t－ブチル－4－メチルフエニル・ブチルカルビトール・ペンタエリスリトールジホスファイト、2,6－ジ－t－ブチル－4－メチルフエニル・オクチルフエニル・ペンタエリスリトールジホスファイト、2,6－ジ－t－ブチル－4－メチルフエニル・ノニルフエニル・ペンタエリスリトールジホスファイト、ビス（2,6－ジ－t－ブチル－4－メチルフエニル）ペンタエリスリトールジホスファイト、ビス（2,6－ジ－t－ブチル－4－エチルフエニル）ペンタエリスリトールジホスファイト、2,6－ジ－t－ブチル－4－メチルフエニル・2,6－ジ－t－ブチルフエニル・ペンタエリスリトールジホスファイト、2,6－ジ－t－ブチル－4－メチルフエニル・2,4－ジ－t－ブチルフエニル・ペンタエリスリトールジホスファイト、2,6－ジ－t－ブチル－4－メチルフエニル・2,4－ジ－t－オクチルフエニル・ペン

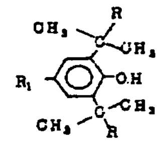
タエリスリトールジホスファイト、2,6－ジ－t－ブチル－4－メチルフエニル・2－シクロヘキシルフエニル・ペンタエリスリトールジホスファイト、2,6－ジ－t－アミル－4－メチルフエニル・フエニル・ペンタエリスリトールジホスファイト、ビス（2,6－ジ－t－アミル－4－メチルフエニル）ペンタエリスリトールジホスファイト、ビス（2,6－ジ－t－オクチル－4－メチルフエニル）ペンタエリスリトールジホスファイトなどがあげられる。

これら有機ホスファイト化合物の添加量は樹脂100重量部に対して0.001～10重量部であり特に0.05～5重量部が好ましい。

本願発明で用いられる前記一般式(I)で示される有機ホスファイト化合物は、例えば



で示されるフエノールと三塩化リンと反応させ、次いでペンタエリスリトール（及びR_2OHで示される化合物）と反応させるか、または三塩化リンに代えてトリフエニルホスファイトまたはトリメチルホスファイトを反応させることによつて製造することができる。また、ジクロロ（またはジメチル、ジフエニル）ペンタエリスリトールジホスファイトと



（及びR_2OH）とを反応させることによつても製造することができる。

次にホスファイト化合物の具体的な合成例を示す。

合成例1　ビス（2,6－ジ－t－ブチル－4－メチルフエニル）ペンタエリスリトールジホスファイトの合成

2,6－ジ－t－ブチル－4－メチルフエノール11.02g（0.05モル）とトリエチルアミン6.10g（0.06モル）をクロロホルム50mlに溶解した。この溶液に室温で三塩化リン6.88g（0.05モル）を滴下後、N_2気流下50℃で9時間反応した。次いでペンタエリスリトール3.41g（0.025モル）とトリエチルアミン16.20g（0.12モル）を加え、N_2気流下55～80℃で9時間反応した。反応後クロロホルムを留去し、これをベンゼンに溶解して、$N(C_2H_5)_3 \cdot HCl$を除去、次いでベンゼンによる再結晶により融点244℃の固体を得た。

本発明の組成物に光安定剤を添加するならば、光安定性を向上させ得るので、使用目的に応じて適宜これらを選択して使用することが可能である。これらにはベンゾフエノン系、ベンゾトリアゾール系、サリシレート系、置換アクリロニトリル系、ピペリジン系、各種の金属塩又は金属キレート、特にニツケル又はクロムの塩又はキレート類、トリアジン系などが包含される。

本発明の組成物に硫黄系抗酸化剤を含有させることもできる。硫黄系抗酸化剤としては、たとえば、ジステアリルチオジプロピオネート、ジラウリルチオジプロピオネート、ペンタエリスリトールテトララウリルチオプロピオネートなどがあげられる。

その他必要に応じて、例えば有機酸金属塩、エポキシ化合物、顔料、充填剤、発泡剤、アミン系抗酸化剤、帯電防止剤、防曇剤、プレートアウト防止剤、表面処理剤、滑剤、難燃剤、螢光剤、防黴剤、殺菌剤、金属不活性化剤、光劣化剤、赤外線吸収剤、加工助剤、離型剤、補強剤などを包含させることができる。

本発明によつて安定化される合成樹脂としては、たとえばポリエチレン、ポリプロピレン、ポリブテン、ポリ－3－メチルブテンなどのα－オレフイン重合体またはエチレン－酢酸ビニル共重合体、エチレン－プロピレン共重合体などのポリオレフインおよびこれらの共重合体、ポリ塩化ビニル、ポリ臭化ビニル、ポリフツ化ビニル、ポリ塩化ビニリデン、塩素化ポリエチレン、塩素化ポリプロピレン、ポリフツ素化ビニリデン、臭素化ポリエチレン、塩化ゴム、塩化ビニル－酢酸ビニル共重合体、塩化ビニル－エチレン共重合体、塩化ビニル－プロピレン共

重合体、塩化ビニル－スチレン共重合体、塩化ビニル－イソブチレン共重合体、塩化ビニル－塩化ビニリデン共重合体、塩化ビニル－スチレン－無水マレイン酸三元共重合体、塩化ビニル－スチレン－アクリロニトリル共重合体、塩化ビニル－ブタジエン共重合体、塩化ビニル－イソプレン共重合体、塩化ビニル－塩素化プロピレン共重合体、塩化ビニル－塩化ビニリデン－酢酸ビニル三元共重合体、塩化ビニル－アクリル酸エステル共重合体、塩化ビニル－マレイン酸エステル共重合体、塩化ビニル－メタクリル酸エステル共重合体、塩化ビニル－アクリロニトリル共重合体、内部可塑化ポリ塩化ビニルなどの含ハロゲン合成樹脂、ポリスチレン、ポリ酢酸ビニル、アクリル樹脂、スチレンと他の単量体（例えば無水マレイン酸、ブタジエン、アクリロニトリルなど）との共重合体、アクリロニトリル－ブタジエン－スチレン共重合体、アクリル酸エステル－ブタジエン－スチレン共重合体、メタクリル酸エステル－ブタジエン－スチレン共重合体、ポリメチルメタクリレートなどのメタクリレート樹脂、ポリビニルアルコール、ポリビニルホルマール、ポリビニルブチラール、直鎖ポリエステル、ポリアミド、ポリカーボネート、ポリアセタール、ポリウレタン、ポリフェニレンオキサイド、繊維素系樹脂、あるいはフェノール樹脂、ユリア樹脂、メラミン樹脂、エポキシ樹脂、不飽和ポリエステル樹脂、シリコーン樹脂などを挙げることができる。更に、イソプレンゴム、ブタジエンゴム、アクリロニトリル－ブタジエン共重合ゴム、スチレン－ブタジエン共重合ゴムなどのゴム類やこれらの樹脂のブレンド品であつてもよい。

また、過酸化物あるいは放射線等によつて架橋させた架橋ポリエチレン等の架橋合成樹脂及び発泡剤によつて発泡させた発泡ポリスチレン等の発泡合成樹脂も包含される。

次に示す実施例は本発明による組成物の効果を示すものであるが、本発明はこれらの実施例によつて限定されるものではない。

実施例1

シス－1,4－イソプレンゴム（チグラー系触媒、数平均分子量680,000）100 gr に対してペンタエリスリトール・テトラキス（3,5－ジ－t－ブチル－4－ヒドロキシフエニルプロピオネート）0.1 gr 及び有機ホスフアイト化合物0.2 gr を添加した後、乾燥させたイソオクタン250 ml を加え、均一な溶液に調製した。次いでこの溶液をエバポレーターに移し温浴上で脱溶媒した。得られたゴム組成物を100℃の恒温槽で3時間熱老化させた。着色テスト、臭気テスト及び固有粘度測定（トルエン溶媒）を行つた。その結果を表－1に示す。

表 － 1

№	有機ホスフアイト化合物	オリジナルの臭気*	劣化後の着色	固有粘度〔η〕オリジナル	固有粘度〔η〕劣化後
参考例					
1－1	な　し	+	褐　色	4.7	測定不可
1－2	トリス（2,4－ジ－t－ブチルフエニル）ホスフアイト	+++++	淡褐色	4.6	3.9
1－3	ビス（2,4－ジ－t－ブチルフエニル）ペンタエリスリトールジホスフアイト	+++	黄　色	4.5	3.7
実施例					
1－1	2,6－ジ－t－ブチル－4－メチルフエニル・フエニルペンタエリスリトールジホスフアイト	+	無　色	4.6	4.4
1－2	2,6－ジ－t－ブチル－4－メチルフエニル・イソオクチルペンタエリスリトールジホスフアイト	+	〃	4.7	4.4
1－3	ビス（2,6－ジ－t－ブチル－4－メチルフエニル）ペンタエリスリトールジホスフアイト	+	〃	4.8	4.5

*臭気テストは無作為に抽出した20人のパネラーにより行ない。
+（臭気小）～ +++++（臭気大）で表わした。

実施例2

スチレン-アクリロニトリル共重合樹脂　100　重量部

1,3,5-トリス(2,6-ジ-メチル-3-ヒドロキシ-4-第3ブチルベンジル)イソシアヌレート　0.05

ホスファイト化合物(表-2)　0.05

上記配合物を230℃で押し出し加工してペレットを作成し、230℃でインジエクションでの滞留試験を行なつた。滞留なし、滞留10分後、滞留20分後に厚さ2㎜の試験片を射出成型し、試験片の着色の度合をハンター比色計で測定した黄色度で示した。

結果を表-2に示す。

表-2

№	ホスファイト化合物	黄色度		
		滞留なし	10分後	20分後
参考例				
2-1	ビス(2,4-ジ-t-ブチル-5-メチルフエニル)ペンタエリスリトールジホスファイト	15	20	33
2-2	ビス(2,6-ジ-t-ブチルフエニル)ペンタエリスリトールジホスファイト	18	22	36
実施例				
2-1	ビス(2,6-ジ-t-ブチル-4-メチルフエニル)ペンタエリスリトールジホスファイト	12	14	18
2-2	ビス(2,6-ジ-t-ブチル-4-エチルフエニル)ペンタエリスリトールジホスファイト	11	13	17
2-3	2,6-ジ-t-ブチル-4-メチルフエニル・シクロヘキシル・ペンタエリスリトールジホスファイト	10	12	15
2-4	2,6-ジ-t-ブチル-4-メチルフエニル・トリデシル・ペンタエリスリトールジホスファイト	10	12	15
2-5	2,6-ジ-t-ブチル-4-メチルフエニル・2-シクロヘキシルフエニル・ペンタエリスリトールジホスファイト	12	15	19

実施例3

ABS樹脂(スタイラック200：旭ダウ)　100　重量部

カルシウムステアレート　1.0

ホスファイト化合物(表-3)　0.3

1,3,5-トリス(3,5-ジ-t-ブチル-4-ヒドロキシベンジル)イソシアヌレート　0.1

上記配合物を200℃で押し出し加工してペレットを作成し、このペレットを用い230℃でインジエクション加工して試験片を作成した。この試験片の135℃のギヤーオーブン中で30時間加熱後の着色の度合をハンター比色計で測定した白色度で示した。さらに試験片の20℃でのIzod衝撃値も測定した。また、100℃の熱水に72時間浸漬した試験片のIzod衝撃値も測定した。結果を表-3に示す。

表-3

№	ホスファイト化合物	白色度	Izod 衝撃値(kg·cm/cm)		
			オリジナル	加熱後	熱水浸漬後
参考例 3-1	ビス(2,4-ジ-t-ブチル-6-メチルフエニル)ペンタエリスリトールジホスファイト	19.9	17.6	13.5	13.5
実施例 3-1	2,6-ジ-t-ブチル-4-メチルフエニル・イソオクチル・ペンタエリスリトールジホスファイト	33.5	18.7	17.2	17.6
3-2	2,6-ジ-t-ブチル-4-メチルフエニル・ステアリル・ペンタエリスリトールジホスファイト	32.5	19.2	17.5	17.8
3-3	2,6-ジ-t-ブチル-4-メチルフエニル・ベンジル・ペンタエリスリトールジホスファイト	32.1	18.0	16.9	16.2
3-4	ビス(2,6-ジ-t-ブチル-4-メチルフエニル)ペンタエリスリトールジホスファイト	35.4	18.5	17.2	16.7
3-5	2,6-ジ-t-ブチル-4-メチルフエニル/ノニルフエニル・ペンタエリスリトールジホスファイト	34.8	18.4	17.0	16.5

実施例4

次の配合物をミキサーで5分間混合したあと、押し出し機でコンパウンドを作成した(シリンダー温度230℃及び240℃、ヘッドダイス温度250℃、回転数20r.p.m)。

このコンパウンドを用いて95×40×1mmの試験片を射出成型機で作成した(シリンダー温度240℃、ノズル温度250℃、射出圧475kg/cm²)。得られた試験片を用いて170℃のギヤーオーブン中で熱安定性を測定し、またハンター比色計を用いて試験片の黄色度(%)を測定した。結果を表-4に示す。

<配　合>

ポリプロピレン樹脂(Profax6501 ハーキユレス社製)	100	重量部
ステアリン酸カルシウム	0.2	
ジラウリルチオジプロピオネート	0.2	
ペンタエリスリトールテトラキス(3,5-ジ-t-ブチル-4-ヒドロキシフエニルプロピオネート)	0.1	
ホスフアイト化合物(表-4)	0.1	

実施例5

下記の配合により、実施例4と同様に試験片を作成し170℃ギヤーオーブン中での熱安定性試験を行なつた。また、ハンター比色計を用いて試験片の黄色度(%)を測定した。結果を表-5に示す。

<配　合>

ポリプロピレン樹脂(Profax6501: ハーキユレス社製)	100	重量部
ステアリン酸カルシウム	0.2	
ジラウリルチオジプロピオネート	0.2	
ビス(2,6-ジ-t-ブチル-4-メチルフエニル)・ペンタエリスリトールジホスフアイト	0.1	
フエノール化合物(表-5)	0.1	

表-4

No.	ホスフアイト化合物	熱安定性	黄色度(%)	
		時間	オリジナル	72時間後
参考例 4-1	ビス(2,6-ジ-t-ブチルフエニル)ペンタエリスリトールジホスフアイト	538	9.0	11.2
実施例 4-1	ビス(2,6-ジ-t-ブチル-4-メチルフエニル)ペンタエリスリトールジホスフアイト	685	7.8	9.1
4-2	ビス(2,6-ジ-t-ブチル-4-エチルフエニル)ペンタエリスリトールジホスフアイト	638	7.9	9.5
4-3	2,6-ジ-t-ブチル-4-メチルフエニル・ブチルカルビトール・ペンタエリスリトールジホスフアイト	653	7.7	9.2
4-4	2,6-ジ-t-ブチル-4-メチルフエニル・ブチルトリグリコール・ペンタエリスリトールジホスフアイト	703	7.9	9.5
4-5	2,6-ジ-t-ブチル-4-エチルフエニル・インデシル・ペンタエリスリトールジホスフアイト	684	7.8	9.4
4-6	2,6-ジ-t-ブチル-4-エチルフエニル・4-t-ブチルフエニル・ペンタエリスリトールジホスフアイト	712	7.6	9.3

表 - 5

𝒩𝑜	フエノール化合物	熱安定性	黄色度 (%)	
参考例		時間	オリジナル	72時間後
5 - 1	な し	2 4	1 2.3	―
実施例				
5 - 1	2,6 - ジ - t - ブチル - 4 - メチルフエノール	9 6	1 0.3	1 5.2
5 - 2	4,4′ - ブチリデンビス (2 - t - ブチル - 5 - メチルフエノール)	1 8 5	9.7	1 2.7
5 - 3	1,1,3 - トリス (2 - メチル - 4 - ヒドロキシ - 5 - t - ブチルフエニル) ブタン	2 1 6	9.8	1 2.4
5 - 4	1,3,5 - トリメチル - 2,4,6 - トリス (3,5 - ジ - t - ブチル - 4 - ヒドロキシベンジル) ベンゼン	3 3 5	9.1	1 1.6
5 - 5	ステアリル - 3,5 - ジ - t - ブチル - 4 - ヒドロキシフエニルプロピオネート	6 4 2	7.7	9.3
5 - 6	チオジエチレングリコールビス (3,5 - ジ - t ブチル - 4 - ヒドロキシフエルプロピオネート)	6 2 8	8.2	9.9
5 - 7	1,6 - ヘキサンジオールビス (3,5 - ジ - t - ブチル - 4 - ヒドロキシフエニルプロピオネート)	6 2 0	7.8	9.6
5 - 8	1,3,5 - トリス (2 - ヒドロキシエチル) イソシアヌレートトリス (3,5 - ジ - t - ブチル - 4 - ヒドロキシフエニルプロピオネート)	6 7 4	8.0	9.2
5 - 9	ペンタエリスリトールテトラキス (3,5 - ジ - t - ブチル - 4 - ヒドロキシフエニルプロピオネート)	6 8 5	7.8	9.1
5-10	1,3,5 - トリス (3,5 - ジ - t - ブチル - 4 - ヒドロキシベンジル) イソシアヌレート	7 1 6	7.6	9.0
5-11	1,3,5 - トリス (2,6 - ジメチル - 4 - t - ブチル - 3 - ヒドロキシベンジル) イソシアヌレート	6 5 0	7.8	9.3

実施例 6

次の配合物を150℃で5分間ミキシングロールで混練し、次いで150℃、180 kg / cm^2 の条件で5分間圧縮成型を行ない、厚さ1.0 mmのシートを作成した。このシートを10×20 mmの試験片として、アルミ箔上、150℃の温度でギヤーオーブン中での熱安定性試験を行なつた。結果を表 - 6に示す。

<配　合>

ポリエチレン樹脂(ハイゼックス5100B 三井石油化学社製)	100	重量部
ジステアリルチオジプロピオネート	0.3	
ステアリル - 3,5 - ジ - t - ブチル - 4 - ヒドロキシフエニルプロピオネート	0.1	
ホスファイト化合物(表 - 6)	0.1	

表 - 6

𝒩𝑜	ホスファイト化合物	劣化時間
		時間
参考例 6 - 1	ビス (2 - t - ブチル - 4,6 - ジメチルフエニル) ペンタエリスリトールジホスファイト	5 2 3
実施例 6 - 1	ビス (2,6 - ジ - t - ブチル - 4 - メチルフエニル) ペンタエリスリトールジホスファイト	6 8 3
6 - 2	2,6 - ジ - t - ブチル - 4 - メチルフエニル・イソトリデシル・ペンタエリスリトールジホスファイト	6 7 5
6 - 3	2,6 - ジ - t - ブチル - 4 - メチルフエニル・2 - エチルヘキシル・ペンタエリスリトールジホスファイト	7 0 2
6 - 4	2,6 - ジ - t - ブチル - 4 - エチルフエニル・ジノニルフエニルペンタエリスリトールジホスファイト	6 4 8
6 - 5	2,6 - ジ - t - ブチル - 4 - エチルフエニル・4 - t - オクチルフエニル・ペンタエリスリトールジホスファイト	6 5 0

実施例7

固有粘度0.56 dl/g(クロロホルム中25℃)のポリ(2,6-ジメチル-1,4-フエニレンオキサイド)50重量部、ポリスチレン47.5重量部、ポリカーボネート2.5重量部、酸化チタン3.0重量部、1,3,5-トリス〔(3,5-ジ-t-ブチル-4-ヒドロキシフエニル)プロピオニルオキシエチル〕イソシアヌレート0.2重量部及びホスファイト化合物0.2重量部を加え、ヘンシエルミキサーにて十分混合し押し出し機でペレット化、次いで射出成型により試験片を作成した。この試片をギヤーオーブン中で125℃、100時間加熱し、伸び及びアイゾッド衝撃値保持率を測定した。結果を表-7に示す。

表-7

No.	ホスファイト化合物	保持率(%)	
		伸び	アイゾット衝撃値
比較例 7-1	ビス(2,4-ジ-t-ブチル-6-メチルフエニル)ペンタエリスリトールジホスファイト	40	53
実施例 7-1	ビス(2,6-ジ-t-ブチル-4-メチルフエニル)ペンタエリスリトールジホスファイト	58	71
7-2	2,6-ジ-t-ブチル-4-メチルフエニル・2,4-ジ-t-ブチルフエニル・ペンタエリスリトールジホスファイト	52	69
7-3	2,6-ジ-t-ブチル-4-メチルフエニル・ラウリル・ペンタエリスリトールジホスファイト	54	75
7-4	2,6-ジ-t-ブチル-4-エチルフエニル・2-フエニルフエニル・ペンタエリスリトールジホスファイト	50	68
7-5	2,6-ジ-t-ブチル-4-エチルフエニル・オレイル・ペンタエリスリトールジホスファイト	54	70

実施例8

ポリカーボネート樹脂	100 重量部
1,6-ヘキサンジオールビス(3,5-ジ-t-ブチル-4-ヒドロキシフエニルプロピオネート)	0.1
ホスファイト化合物(表-8)	0.1

上記配合物を260℃でプレスして厚さ1.0㎜の無色の試験片を作成した。このシートを用いて230℃のギヤーオーブン中で30分間加熱後の試験片の変色の程度を観察した。結果を表-8に示す。

表-8

	ホスファイト化合物	試験片の色
参考例 8-1	ビス(2,4-ジ-t-ブチルフエニル)ペンタエリスリトールジホスファイト	黄色
実施例 8-1	ビス(2,6-ジ-t-ブチル-4-メチルフエニル)ペンタエリスリトールジホスファイト	無色
8-2	ビス(2,6-ジ-t-ブチル-4-エチルフエニル)ペンタエリスリトールジホスファイト	〃
8-3	2,6-ジ-t-ブチル-4-メチルフエニル・イソデシル・ペンタエリスリトールジホスファイト	〃

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(54) **2,6-Di-tertiary butyl phenyl pentaerythritol spiro bis-phosphites enhancing the stability to heat and light of synthetic resins, stabilizer compositions comprising phenolic antioxidants and such phosphites, and synthetic resin compositions containing the same.**

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Description

Polypropylene and other polyolefins such as polyethylene, polybutylene and polyisopentylene show a strong tendency to deteriorate in physical properties at elevated temperatures and when exposed to ultraviolet light. The deterioration is evidenced by, among other things, a decrease in viscosity, a tendency to become brittle, and a discoloration which is particularly pronounced at the exposed edge of the material. This deterioration can be accompanied by distortion, cracking, and powdering of the material. The deterioration is accentuated in the presence of oxygen.

To overcome these difficulties, many stabilizer systems have been proposed for combination with polyolefins, with varying degrees of success. No single stabilizer has proved adequate, and combinations of stabilizers are consequently used almost exclusively. Most stabilized polyolefins on the market contain one or more of such stabilizer combinations. The deterioration appears to be due to a combination of factors, and a combination of stabilizers is therefore more capable of coping with the various types of deterioration. However, the retention of good physical properties over long periods of time remains rather difficult to achieve.

Of the many stabilizer systems that have been proposed, one particularly satisfactory stabilizer system is described in US—PS 3 255 136. This stabilizer system comprises three stabilizers: an organic mono- or polyhydric phenol, an organic phosphite, and a thiodipropionic acid ester. An additional fourth ingredient, which is preferred but not essential, is a polyvalent metal salt of an organic acid. These three and four stabilizers together give an enhanced stabilization which is not obtainable from any of them alone, or in combinations of two.

In these combinations, the phenol alone gives an improved resistance to embrittlement and reduction in melt viscosity of polypropylene at elevated temperatures, but little assistance as to maintenance of color. The phosphite alone is a rather poor stabilizer in preventing deterioration in the first two properties, but it does assist in resisting discoloration. The two together are worse than the phenol alone in every respect except color, which is intermediate.

The thiodipropionic acid ester by itself only improves resistance to embrittlement. The polyvalent metal salt of an organic acid by itself only prevents discoloration. In combinations with the phenol, the color is worse than with the salt alone, and combinations with phosphite only, discoloration is prevented. The effectiveness of all three or four ingredients taken together against all of these types of deterioration is therefore particularly surprising.

The organic phosphite can be any organic phosphite having the formula $(RA)_3$—P, in which A can be oxygen or sulfur or a mixture of the same, and R is aryl, alkyl, cycloalkyl, aralkyl or aralkaryl in any combination. A variety of tris-alkaryl phosphites are disclosed, such as tris-(tertiary-octyl-phenyl)phosphite and tris-(tertiary-nonyl-phenyl)phosphite, but no tris-(alkaryl)phosphites having more than two alkyl groups per phenyl group.

Organic phosphites have been widely used as stabilizers for polyolefins and similar polymeric materials, and many different types of phosphites, some of rather complex structure, have been proposed. US—PS 3 255 136 and 3 655 832 have suggested organic phosphite-phenol transesterification products, the preferred phenol being a bis-phenol. Other types of tris-(alkaryl)phosphite esters have been disclosed in US—PS 2 220 113; 2 220 845; 2 246 059; 2 419 354; 2 612 488; 2 732 365; 2 733 226 and 2 877 259. Additional tris-(alkaryl)phosphites are disclosed in US—PS 3 167 526; 3 061 583; and 3 829 396; FR—PS 1 496 563 and 1 497 390; GB—PS 1 058 977 and 1 143 375.

US—PS 3 829 396 discloses bis-(2,4-di-tertiary-butylphenyl) cyclohexyl phosphite and 2,4-di-(tertiary butyl) phenyl dicyclohexyl phosphite, which are liquids.

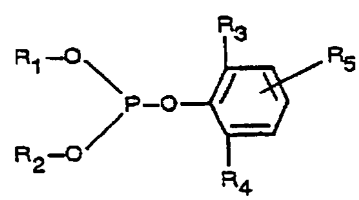
FR—PS 1,496,563 describes phosphites derived from 2,6-di-tertiary-butyl-hydroquinone and 2,5-di-tertiary-butyl-hydroquinone, and it is suggested that they can be used with thiodipropionic acid esters of olefin polymers.

GB—PS 1,143 375 has a similar disclosure; tris-(2,5-di-tertiary-butyl-4-hydroxy-phenyl)phosphite is disclosed.

GB—PS 1,058,977 discloses 2,4,6-tri-substituted aryl phosphites, the substituents including tertiary-butyl groups.

FR—PS 1,497,390 discloses tris-(3,5-di-alkyl-4-hydroxy-phenyl)phosphites, as well as tris-(3-isopropyl-5-tertiary-butyl-phenyl)phosphite.

US—PS 3,558,554 provides olefin polymer compositions containing as a stabilizer an organophosphite having the general formula:



wherein

R_1 and R_2 each represents a member selected from the group consisting of substituted and unsubstituted alkyl, cycloalkyl, aryl, alkaryl, aralkyl, and aliphatic thio ether groups and R_3, R_4 and R_5 each represents a member selected from the group consisting of hydrogen and alkyl, cycloalkyl, aryl, alkaryl, and aralkyl groups, at least one of said R_3 and R_4 being a tertiary butyl group.

Suitable organo phosphites include, for example, di-n-butyl (2-t-butyl-cresyl)phosphite, di-n-hexyl(2-t-butyl-m-cresyl)phosphite, di-n-hexyl(2-t-butyl-p-cresyl)phosphite, di-n-octyl(2-t-butyl-p-cresyl)phosphite, di - n - butyl - 3,4 - di - t - butyl - phenyl)phosphite, di - n - butyl - (2,6 - di - t - butyl-p-cresyl)phosphite, di-phenyl-(2-t-butyl-p-cresyl)phosphite, tri-(2-t-butyl-p-cresyl)phosphite, di-(ethyl-thioethyl)-(2-t-butyl-p-cresyl)phosphite, di(octylthioethyl) (2-t-butyl-p-cresyl)phosphite, and tri(2,4-di-t-butyl-phenyl)phosphite.

Many organic phosphites have been proposed as stabilizers for polyvinyl chloride resins, and are employed either alone or in conjunction with other stabilizing compounds, such as polyvalent metal salts of fatty acids and alkyl phenols. Such phosphite stabilizers normally contain alkyl or aryl radicals in sufficient number to satisfy the three valences of the phosphite, and typical phosphites are described in the patent literature, for example, US—PS 2,564,646, 2,716,092 and 2,997,454.

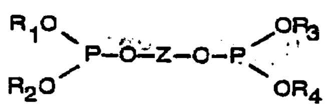
Organic phosphites have also been added as stabilizers in amounts of 0.01 to 1%, preferably 0.05% to 0.2% by weight, to high molecular weight polycarbonate plastics, for example the polycarbonate of 2,2'-bis(4-hydroxyphenyl)propane of molecular weight 10000 and up to over 50000 as disclosed by US—PS 3,305,520.

US—PS 2,860,115 discloses compositions of organic phosphites with metal salts of carboxylic acids used in olefin polymers.

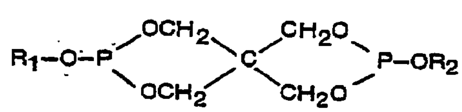
Phosphites are also employed in conjunction with other stabilizers such as a polyhydric phenol in the stabilization of polypropylene and other synthetic resins against degradation upon heating or ageing under atmospheric conditions. The polyhydric phenol is thought to function as an antioxidant in such combinations. Disclosures by US—PS 2,726,226, 2,985,617, 3,039,993, 3,080,338, 3,082,187, 3,115,465, 3,167,526, 3,149,093, 3,244,650, 3,225,136, 3,255,151, 3,352,820, 3,535,277, 3,586,657, 3,856,728, 3,869,423 and 3,907,517 and GB—PS 846,684, 851,670 and 866,883 are representative of stabilizer combinations including organic phosphites, polyhydric phenols, and other active ingredients.

The importance of organic phosphites are stabilizers for synthetic resins has led to the development of a large variety of special phosphites intended to provide improved stabilizing effectiveness and compatibility and ease of compounding with the resin and with other stabilizers commonly used. However, the phosphites which have been proposed have not been entirely successful, partly because of their complicated structure, which makes them costly to prepare, and partly because of their difficulty of preparation.

Among these special phosphites, US—PS 3,047,608 discloses a class of biphosphites having the formula:

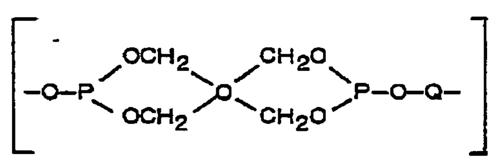


and



in which

R_1, R_2, R_3 and R_4 are alkyl or aryl and Z is $—CH_2CH_2SCH_2CH_2O—$, $—C_2CH_2SO_2C_2CH_2—(CH_2CH_2O)—_x$ or $(CHCH_3CH_2)_x$ where x is at least two, and in US—PS 3,053,878 a class of linear phosphite polymers having the formula:



in which

Q is the alkylene or arylene portion of a dihydric alcohol or dihydric phenol.

US—PS 3,112,286 discloses phosphites having the formula:

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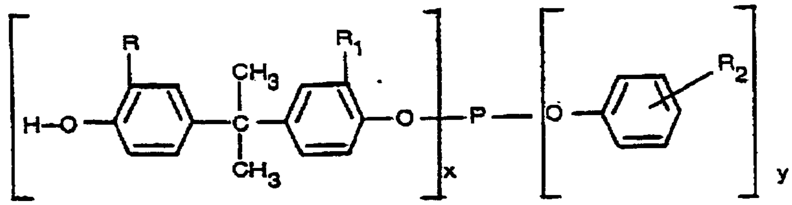


in which

R represents a bulky hydrocarbon group such as t-butyl, t-amyl, t-hexyl, cyclohexyl, t-pentyl, t-octyl, phenyl and the like;

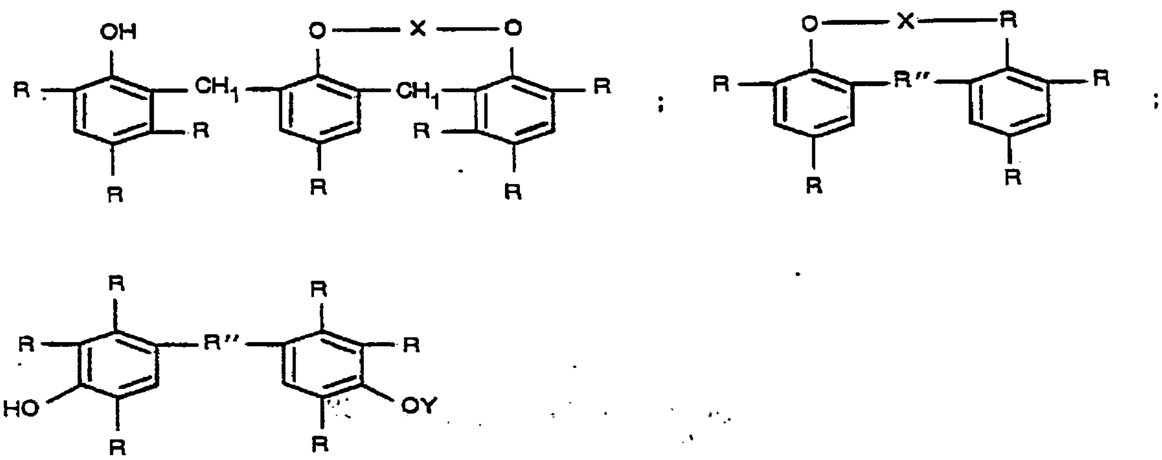
R_1 represents hydrogen and R;

R_3 represents an alkyl group from six to twenty carbon atoms which is preferably in the meta or para position;

x represents a number of from 1 to 3 inclusive;

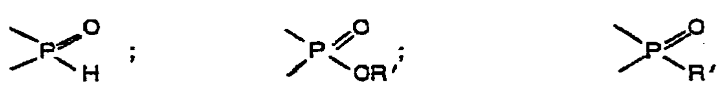
y represents a number of from 0 to 2 inclusive and the sum of the numerical value of x + y is always exactly 3.

US—PS 3,297,631 discloses condensation products of phosphorus compounds with bisphenols and trisphenols which may be represented by the structures:

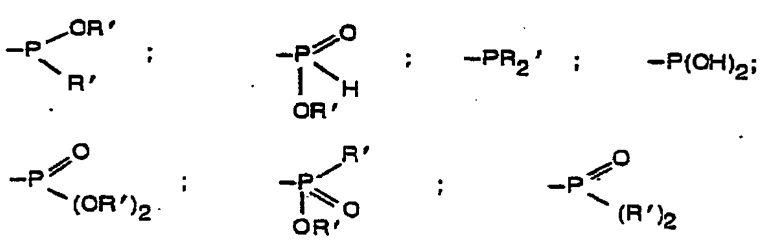


where:

X is selected from the following: >P—OR'; >P—R';



and Y is selected from the following: —P(OR')$_2$;

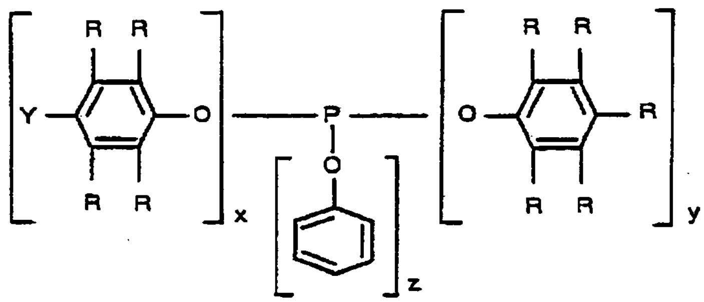


R is hydrogen, alkyl of one to sixteen carbon atoms or aryl or a combination of these; R' is alkyl of one to

sixteen carbon atoms or aryl, and R'' is alkylidene of one to sixteen carbon atoms or an aryl-substituted alkylidene.

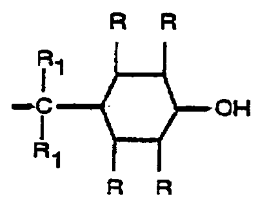
US—PS 3,305,608 discloses phenolic phosphites useful as polymer stabilizers prepared by reacting a triorganophosphite, a polyol, and an aromatic material having two to six phenolic hydroxyl groups at 60° to 180°C in specified proportions.

US—PS 3,412,064 discloses phenolic phosphites represented by the general formula:



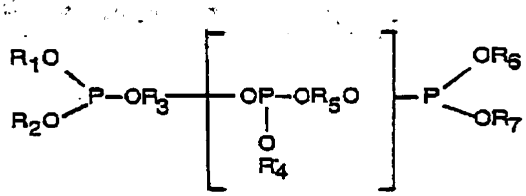
where

x is from 1 to 3, y and z each from 0 to 2, x + y + z = 3, R is hydrogen or alkyl and Y is hydroxyl or a group of the formula:



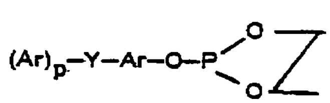
where R is hydrogen or alkyl.

US—PS 3,419,524 discloses phosphites useful as polymer stabilizers having the formula:



where R_1, R_2, R_4, R_6 and R_7 are aryl or haloaryl, and R_3 and R_5 are a polyalkylidene glycol or an alkylidene bisphenol or a hydrogenated alkylidene bisphenol or a ring-halogenated alkylidene bisphenol from which the two terminal hydrogens have been removed.

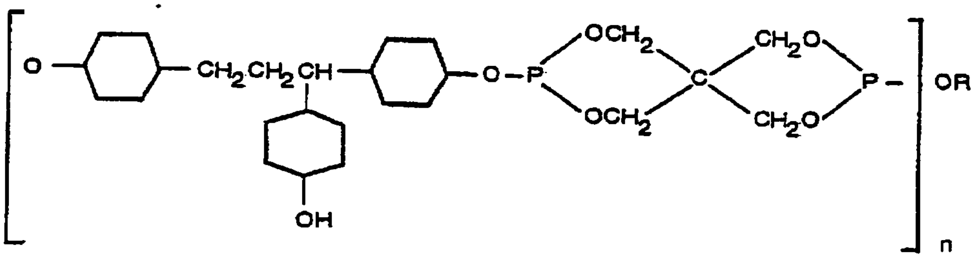
US—PS 3,476,699 and 3,655,832 disclose organic phosphites containing a free phenolic hydroxyl group and defined by the formula:



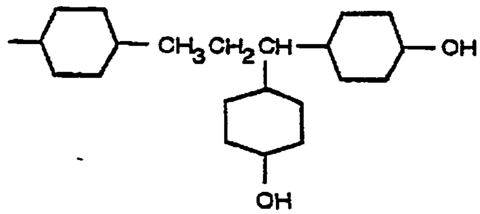
wherein Z is selected from the group consisting of hydrogen and aliphatic, cycloaliphatic, aromatic, heterocyclic and $(Ar)_p$—Y—Ar groups, taken in sufficient number to satisfy the valences of the two phosphite oxygen atoms; Y is a polyvalent linking group selected from the group consisting of oxygen; aliphatic, cycloaliphatic and aromatic hydrocarbon groups attached to each Ar group through a carbon atom not a member of an aromatic ring; oxyaliphatic; thioaliphatic, oxycycloaliphatic, thiocycloaliphatic; heterocyclic, oxyheterocyclic, thioheterocyclic, carbonyl, sulfinyl; and sulfonyl groups; Ar is a phenolic

nucleus which can be phenyl or a polycarbocyclic group having condensed or separate phenyl rings; each Ar group is either connected through an oxygen atom to a phosphite group or contains a free phenolic hydroxyl group, or both; and p is a number, one or greater, and preferably from one to four, which defines the number of Ar groups linked to Y.

US—PS 3,516,963 discloses phosphites having the formula:

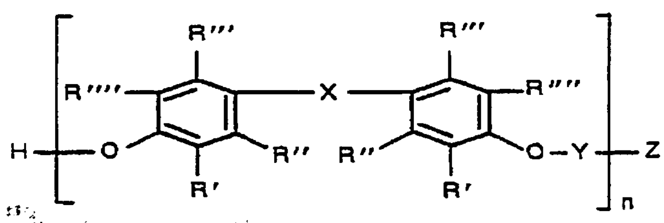


where R is alkyl, alkenyl, aryl, aralkyl, haloaryl, haloalkyl or



and n is an integer of at least 1. n can be 2, 3, 4, 5, 6, 7, 8, 10, 50, 100 or even more.

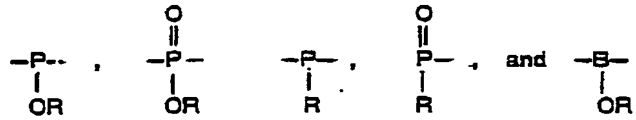
US—PS 3,510,507 and 3,691,132 disclose polyolefins stabilized with polyphosphites, polyphosphates, polyphosphonites, polyphosphonates, polyborates, polycarbonates, and polysilanes which are condensation products of a 4,4'-bisphenol with a condensing or linking agent which may be of the ester type, such as the esters of triaryl or mixed aryl-alkyl compounds, or the acid halide type. The above-described condensation product stabilizers have molecular weights between 600 and 8000 or higher and are described by the structural formula:



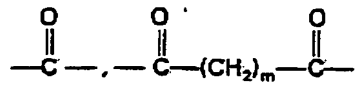
where X is selected from the group consisting of

$$—S—,\quad —\overset{R}{\underset{R}{\overset{|}{\underset{|}{C}}}}—,\quad —\overset{O}{\overset{\|}{C}}—,$$

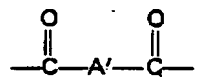
—C—C, and C—A—C— where A is a C_1 to C_{16} alkylene or an arylene; R', R", R"', and R"" are selected from the group consisting of hydrogen, C_1 to C_{18} alkyls, and an aryl group; Y is selected from the group of



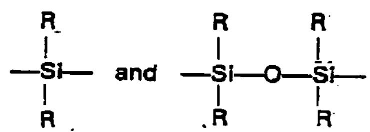
where R is hydrogen, a C_1 to C_{18} alkyl or aryl;



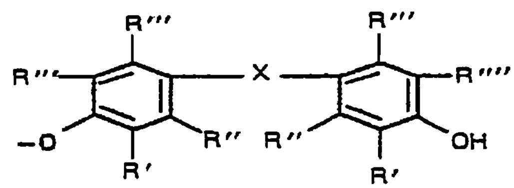
where m is 0 to 10, preferably 4 to 8,



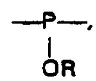
where A' is $(CH_2)_n$—S—$(CH_2)_n$ or —$(CH_2)_n$—S—$(CH_2)_m$—S—$(CH_2)_n$ where n is 0 to 10, preferably 2 and m is 0 to 10, preferably 5;



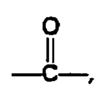
where R is an alkyl, preferably methyl, and Z is



where R', R'', R''', R'''', and X correspond respectively to the R', R'', R''', R'''', and X previously selected when n has a value from 1 to 15, or may be derived from the compound used to introduce Y into the product when n has a value from 2 to 15, for example, —R or —OR where R is hydrogen, an alkyl, or aryl. When Y in the above formula of stabilizer is



the stabilizer is a type of hydroxyaryl phosphite. Similarly, when Y in the formula is



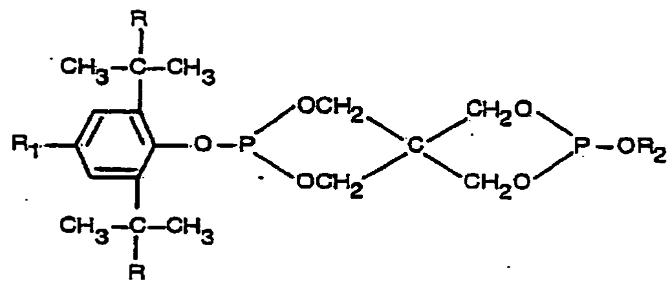
the stabilizer is a hydroxyaryl carbonate.

The above described condensation products are described as especially effective in high molecular weight solid polyolefins when used together with a dialkyl sulfide costabilizer such as dilauryl thiodipropionate, distearyl thiodipropionate, ditridecyl thiodipropionate, dicetyl sulfide, bis(tetradecylmercapto)paraxylylene, and 10,24-dithiotetracontane.

DE—OS 2505071 (abstracted in *Chemical Abstracts* 1976, Volume 84, abstract No. 5945f) discloses low molecular weight polycarbonate esters of bisphenols such as 2,2-bis(3-t-butyl-4-hydroxyphenylpropane) and 4,4'-butylidene bis(6-t-butyl-3-methylphenol) prepared in such a way as to contain few or no free phenolic hydroxyl groups as being highly effective heat and light stabilizers for

polyolefins and giving a synergistic effect with distearyl thiodipropionate, tris (nonylphenyl)phosphite, and distearyl pentaerythritol diphosphite.

In accordance with the present invention, there are provided 2,6-di-tertiary-butyl phenyl pentaerythritol spiro bis-phosphites having the general structure:



wherein:

R is alkyl having from one to six carbon atoms;

R_1 is methyl or ethyl;

R_2 is selected from alkyl having from 1 to 18 carbon atoms; cycloalkyl having from 3 to 12 carbon atoms; and alkaryl and aryl having from 6 to 30 carbon atoms; such groups substituted with from 1 to 4 oxy ether(—O—) and/or carboxylic ester groups; the residue of a polyhydric alcohol having from 2 to 18 carbon atoms, and from 2 to 10 hydroxyl groups, the residue R_2 being bond to the phosphorus atom by an oxy group of a hydroxyl group; and the residue of a polyphenol having from 6 to 18 carbon atoms and from 2 to 10 phenolic hydroxyl groups, the residue R_2 being bond to the phosphorus atom by an oxy group of a phenolic group and R_2 may be a benzyl radical when R is a methyl radical and R_1 is an ethyl radical.

Stabilizer compositions are provided comprising a phenolic antioxidant and such phosphites as well as synthetic resin compositions having an enhanced resistance to deterioration by heat and/or light due to the presence of such a phosphite and/or stabilizer composition.

These phosphites and stabilizer compositions are capable of enhancing the resistance to deterioration due to heat and/or light of synthetic resins such as a class, when combined therewith in small amounts, within the range from 0.01 to 5% of the phosphite and from 0.01 to 10% of the stabilizer composition, by weight of the synthetic resin.

Exemplary R and R_2 alkyl groups include, for example, methyl, ethyl, propyl, isopropyl, butyl, secondary butyl, tertiary butyl, isobutyl, amyl, isoamyl, secondary amyl, 2,2-dimethyl propyl, tertiary amyl, hexyl, isohexyl, heptyl, octyl, 2-ethyl hexyl, isooctyl, nonyl, isononyl, decyl, isodecyl, lauryl, myristyl, palmityl and stearyl.

R_2 may also be cycloalkyl having 3 to 12 carbon atoms, including, for example, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclododecyl and alkyl-substituted cycloalkyl such as 4-methylcyclohexyl, 4-methylcyclopentyl, and p-dimethylcyclohexyl.

R_2 alkaryl and aryl groups include phenyl, diphenyl, naphthyl, tolyl, xylyl, ethylphenyl, butylphenyl, tertiary butylphenyl, octylphenyl, 2,6 - di - t - butyl - 4 - methylphenyl, 2,6 - di - t - butyl - 4 - (2 - methoxycarbonylethyl)phenyl, isooctylphenyl, t - octylphenyl, nonylphenyl, 2,4 - di - t - butylphenyl, cyclohexylphenyl, cyclooctylphenyl, 4 - methoxyphenyl, 4 - ethoxyphenyl, 3 - lauryloxyphenyl, 2 - methoxy - 4 - methylphenyl, 2 - t - butyl - 4 - methoxyphenyl, 4 - benzyloxyphenyl, and 3,4 - methylenedioxyphenyl.

Examples of R_2 alkyl and alkaryl including ether and carboxylic acid ester groups include 2,6-di-t-butyl-4-(2-methoxycarbonylethyl)phenyl, 4-methoxyphenyl, 4-ethoxyphenyl, 3-lauroxyphenyl, 2-methoxy-4-methylphenyl, 2-t-butyl-4-methoxyphenyl, 4-benzyloxyphenyl, and 3,4-methylenedioxyphenyl.

R_2 can also be the radical derived from a polyhydric alcohol or polyphenol having at 2 to 10 alcoholic or phenolic hydroxyl groups capable of being esterified with trivalent phosphorus of a phosphite, of which at least one such group (—O—) is bond to the phosphorus atom and the remaining hydroxy group or groups may be taken up with a phosphorus atom of another molecule of the diphosphite or may be free, such as, radicals derived from ethylene glycol, glycerol, erythritol, pentaerythritol, sorbitol, mannitol, dulcitol, trimethylol ethane, trimethylol propane, trimethylol butane, 1,2-propanediol, 1,3-propanediol, 1,2-butanediol, 1,4-butanediol, neopentylglycol, thiodiethyleneglycol, 1,6-hexanediol, 1,10-decanediol, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, 1,4-phenylenedimethanol, hydrogenated Bisphenol A, glycerine, trimethylolethane, trimethylolpropane, tris(2-hydroxyethyl)isocyanurate.

Also included are the said radicals derived from polyoxyalkylene polyols containing one or more oxyalkylene groups with terminal hydroxyls free or etherified with alkyl, cycloalkyl or phenyl groups

having from 1 to 10 carbon atoms. Exemplifying this class are methyl Cellosolve®, ethyl Cellosolve®, isopropyl Cellosolve®, butyl Cellosolve®, hexyl Cellosolve®, cyclohexyl Cellosolve®, and phenyl Cellosolve®, methyl Carbitol®, ethyl Carbitol®, isopropyl Carbitol®, butyl Carbitol®, and isobutyl Carbitol®, dipropylene glycol, diethylene glycol, triethylene glycol, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, triethylene glycol monobutyl ether, glyceryl 1,2-dimethyl ether, glyceryl 1,3-dimethyl ether, glyceryl 1,3-diethyl ether and glyceryl 1-ethyl-2-propyl ether; nonyl phenoxy; polyethoxy ethyl, and lauryloxy polyethoxyethyl.

Exemplary polyhydric phenols from which the radicals may be derived include hydroquinone, 2,5 - di - t - butylhydroquinone, 2,3,6 - trimethylhydroquinone, 2 - methylresorcinol, 2,6 - di - t - butylresorcinol, 2,2′ - methylenebis (4 - methyl - 6 - t - butylphenol), 2,2′ - methylenebis(4 - ethyl - 6 - t - butyl - phenol), 2,2′ - methylenebis[4 - methyl - 6 - (-methylcyclohexyl)phenol], 2,2′ - n - butylidenebis(4,6 - dimethylphenyl), 1,1 - bis - (2′ - hydroxy - 3′,5′ - dimethylphenyl) - 3,5,5 - trimethylhexane, 2,2′ - cyclohexylidenebis(4 - ethyl - 6 - t - butylphenol), 2,2′ - thiobis(4 - t - butyl - 6 - methylphenol), 2,2′ - isopropylidene bis(4 - t - butyl - 6 - methylphenol), 1,4 - benzylidenebis(4 - ethyl - 6 - t - butylphenol), 2,2′ - thiobis(4 - methyl - 6 - t - butylphenol), 2,2′ - thiobis(4,6 - di - t - butylphenol), 4,4′ - methylene bis(2 - methyl - 6 - t - butylphenol), Bisphenol A, 4,4′ - isopropylidenebis (2 - phenylethylphenol), 4,4′ - n - butylidenebis(3 - methyl- 6 - t - butylphenol), 4,4′ - cyclohexylidenebisphenol, 4,4′ - cyclohexylidenebis (2 - t - butyl - phenol), 4,4′ - cyclohexylidenebis(2 - cyclohexylphenol), 4,4′ - benzylidenebis(2 - t - butyl - 5 - methyl- phenol), 4,4′ - oxabis(3 - methyl - 6 - isopropylphenol), 4,4′ - thiobis(3 - methyl - 6 - t - butylphenol), 4,4′ - sulfobis(3 - methyl - 6 - t - butylphenol), bis(2 - methyl - 4 - hydroxy - 5 - t - butylbenzyl)sulfide, and 1,1,3 - tris(2′ - methyl - 4′ - hydroxy - 5′ - t - butylphenyl)butane.

Exemplary 2,6 - di - t - butylphenyl pentaerythritol spiro bisphosphites useful with phenolic antioxidants in accordance with the invention include 2,6 - di - t - butyl - 4 - methyl isotridecyl pentaerythritol di-phosphate, 2,6 - di - t - butyl - 4 - ethylphenyl 2 - ethylhexyl pentaerythritol diphosphite, 2,6 - di - t - butyl - 4 - methylphenyl phenyl pentaerythritol diphosphite, 2,6 - di - t - butyl - 4 - methylphenyl methyl pentaerythritol diphosphite, 2,6 - di - t - butyl - 4 - methylphenyl - 2 - ethylhexyl pentaerythritol diphosphite, 2,6 - di - t - butyl - 4 - methylphenyl isodecyl pentaerythritol diphosphite, 2,6 - di - t - butyl - 4 - ethylphenyl lauryl pentaerythritol diphosphite, 2,6 - di - t - butyl - 4 - ethylphenyl isotridecyl pentaerythritol diphosphite, 2,6 - di - t - butyl - 4 - methylphenyl stearyl pentaerythritol diphosphite, 2,6 - di - t - butyl - 4 - methylphenyl cyclohexyl pentaerythritol diphosphite, 2,6 - di - t - butyl - 4 - ethylphenyl benzyl pentaerythritol diphosphite, 2,6 - di - t - butyl - 4 - methylphenyl 2 - ethoxyethyl pentaerythritol diphosphite, 2,6 - di - t - butyl - 4 - methylphenyl 3,6 - dioxadecyl pentaerythritol diphosphite, 2,6 - di - t - butyl - 4 - methylphenyl octylphenyl pentaerythritol diphosphite, 2,6 - di - t - butyl - 4 - methylphenyl nonylphenyl pentaerythritol diphosphite, bis(2,6 - di - t - butyl - 4 - methylphenyl) pentaerythritol diphosphite, bis(2,6 - di - t - butyl - 4 - ethylphenyl) pentaerythritol diphosphite, 2,6 - di - t - butyl - 4 - methylphenyl - 2,6 - di - t - butylphenyl pentaerythritol diphosphite, 2,6 - di - t - butyl - 4 - methylphenyl - 2,4 - di - t - butylphenyl pentaerythritol diphosphite, 2,6 - di - t - butyl - 4 - methylphenyl - 2,4 - di - t - octylphenyl pentaerythritol diphosphite, 2,6 - di - t - butyl - 4 - methylphenyl - 2 - cyclohexylphenyl pentaerythritol diphosphite, 2,6 - di - t - amyl - 4 - methylphenyl phenyl pentaerythritol diphosphite, bis(2,6 - di - t - amyl - 4 - methylphenyl) pentaerythritol diphosphite, bis(2,6 - di - t - amyl - 4 - methylphenyl) pentaerythritol diphosphite.

These phosphites are readily prepared by conventional procedures. Thus, for example, the corresponding 2,6-di-t-butyl-4-methyl or ethyl phenol can be reacted with phosphorus trichloride or a triphosphite such as trimethyl phosphite or triphenyl phosphite, pentaerythritol, and R_2OH in the presence of a base, such as an amine catalyst, to form the phosphite.

The following Example serves to illustrate the procedure:

Example I

Synthesis of bis(2,6-di-t-butyl-4-methylphenyl)pentaerythritol diphosphite.

2,6-Di-t-butyl-4-methylphenol 11.02 g (0.05 mole) and triethylamine 6.1 g (0.06 mole) were dissolved in 50 ml of chloroform and then PCl_3 6.88 g (0.05 mole) was added dropwise at room temperature.

The reaction mixture was heated at 50°C for nine hours. Pentaerythritol 3.41 g (0.025 mole) and triethylamine 16.2 g (0.12 mole) were then added and the reaction mixture heated an additional nine hours at 55 to 80°C under a stream of nitrogen. Then, solvent was distilled off, and 100 ml of benzene was added. The precipitated triethylamine hydrochloride was filtered and the benzene was evaporated.

The residual solid was recrystallized from benzene, and a white powder of m.p. 244°C was obtained.

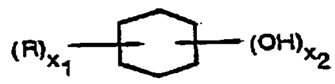
The phenolic antioxidant component of the stabilizer composition of the invention can be a liquid or a solid, and contains one or more phenolic hydroxyl groups, and one or more phenolic nuclei, and can contain from 8 to 300 carbon atoms. In addition, the phenolic nucleus can contain an oxy or thio ether group.

The alkyl-substituted phenols and polynuclear phenols, because of their molecular weight, have a

higher boiling point and therefore are preferred because of their lower volatility. There can be one or a plurality of alkyl groups of one or more carbon atoms. The alkyl group or groups including any alkylene groups between phenol nuclei preferably aggregate at least four carbon atoms. The longer the alkyl or alkylene chain, the better the compatibility with the liquid stabilizer system, and therefore there is no upper limit on the number of alkyl carbon atoms. Usually from the standpoint of availability, the compound will not have more than eighteen carbon atoms in an alkyl, alicyclidene and alkylene group, and a total of not over fifty carbon atoms. The compounds may have from one to four alkyl radicals per phenol nucleus.

The phenol contains at least one and preferably at least two phenolic hydroxyls, the two or more hydroxyls being in the same ring, if there is only one. In the case of bicyclic phenols, the rings can be linked by thio or oxyether groups, or by alkylene, alicyclidene or arylidene groups.

The monocyclic phenols which can be employed have the structure:



R is selected from the group consisting of hydrogen; halogen; and organic radicals containing from 1 to 30 carbon atoms, such as alkyl, aryl, alkenyl, alkaryl, aralkyl, cycloalkenyl, cycloalkyl, alkoxy, and acyl

$$(R'\underset{\underset{O}{\|}}{C}—),$$

where R′ is aryl, alkyl or cycloalkyl;

x_1 and x_2 are integers from one to four, and the sum of x_1 and x_2 does not exceed six.

The polycyclic phenol employed in the stabilizer combination is one having at least two aromatic nuclei linked by a polyvalent linking radical, as defined by the formula:

$$\begin{array}{ccc} (Ar)_{n_1} & —Y— & (Ar)_{n_2} \\ | & & | \\ (OH)_{m_1} & & (OH)_{m_2} \end{array}$$

wherein:

Y is a polyvalent linking group selected from oxygen; carbonyl; sulfur; sulfinyl; aromatic, aliphatic and cycloaliphatic hydrocarbon groups; and oxyhydrocarbon, thiohydrocarbon and heterocyclic groups. The linking group can have from 1 to 20 carbon atoms.

Ar is a phenolic nucleus which can be a phenyl or a polycarbocyclic group having condensed or separate phenyl rings; each Ar group contains at least one free phenolic hydroxyl group up to a total of five. The Ar rings can also include additional rings connected by additional linking nuclei of the type Y, for example, Ar—Y—Ar—Y—Ar.

m_1 and m_2 are numbers from one to five, and n_1 and n_2 are numbers of one or greater, and preferably from one to four.

The aromatic nucleus Ar can, in addition to phenolic hydroxyl groups, include one or more inert substituents. Examples of such inert substituents include halogen atoms, e.g., chlorine, bromine and fluorine; organic radicals containing from 1 to 30 carbon atoms, such as alkyl, aryl, alkaryl, aralkyl, cycloalkenyl, cycloalkyl, alkoxy, aryloxy and acyloxy

$$(R'\underset{\underset{O}{\|}}{C}—O)$$

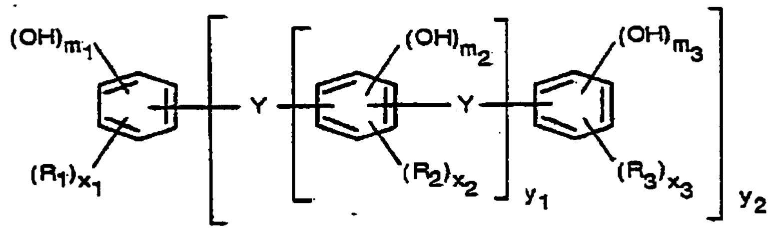
where R′ is aryl, alkyl or cycloalkyl, or thiohydrocarbon groups having from 1 to 30 carbon atoms, and carboxyl

$$(—\underset{\underset{O}{\|}}{C}—O—)$$

groups. Usually, however, each aromatic nucleus will not have more than eighteen carbon atoms in any hydrocarbon substituent group. The Ar group can have from one to four substituent groups per nucleus.

Typical aromatic nuclei include phenyl, naphthyl, phenanthryl, triphenylenyl, anthracenyl, pyrenyl, chrysenyl, and fluorenyl groups.

When Ar is a benzene nucleus, the polyhydric polycyclic phenol has the structure:



wherein

R_1, R_2 and R_3 are inert substituent groups selected from the group consisting of halogen, alkyl, aryl, alkaryl, aralkyl, cycloalkenyl, cycloalkyl, alkoxy, aryloxy and acyloxy

$$\left(R'\underset{\underset{O}{\|}}{C}\text{—}O\right)$$

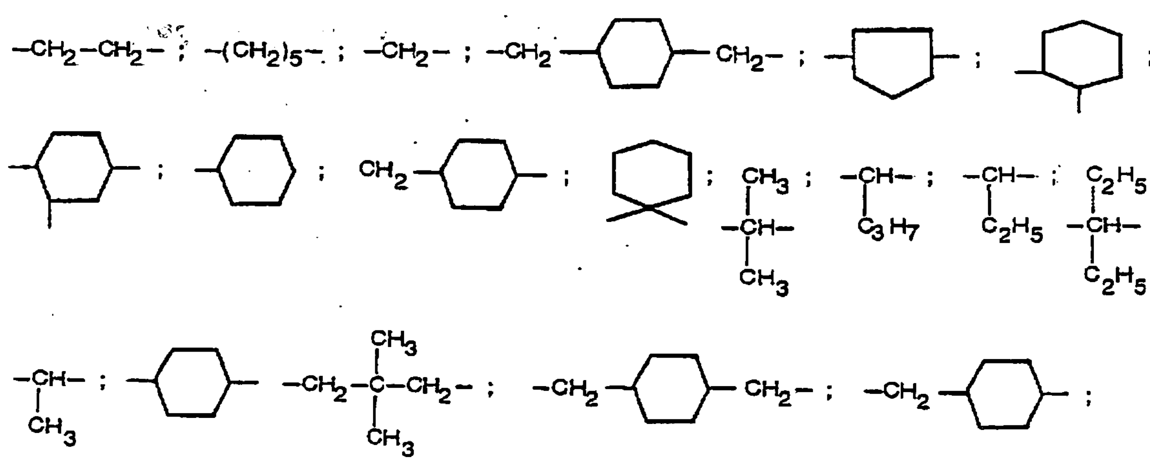
where R′ is aryl, alkyl, or cycloalkyl containing from 1 to 30 carbon atoms; thiohydrocarbon groups having from 1 to 30 carbon atoms, and carboxyl groups;

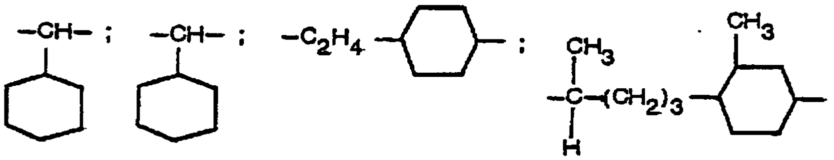
m_1 and m_3 are integers from one to a maximum of five;
m_2 is an integer from one to a maximum of four;
x_1 and x_3 are integers from zero to four; and
x_2 is an integer from zero to three;
y_1 is an integer from zero to six; and
y_2 is an integer from one to five, preferably one or two.

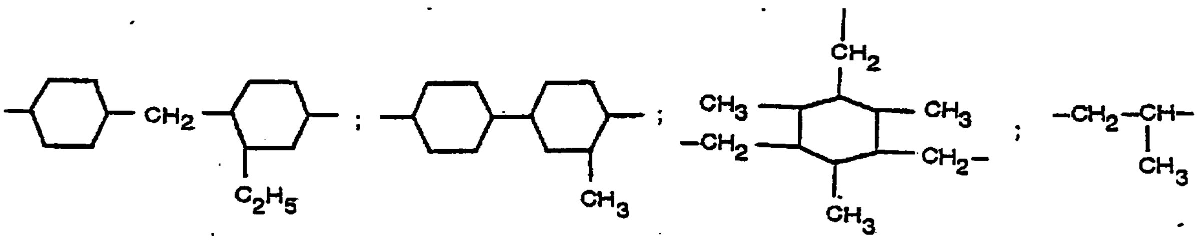
Preferably, the hydroxyl groups are located ortho and/or para to Y.

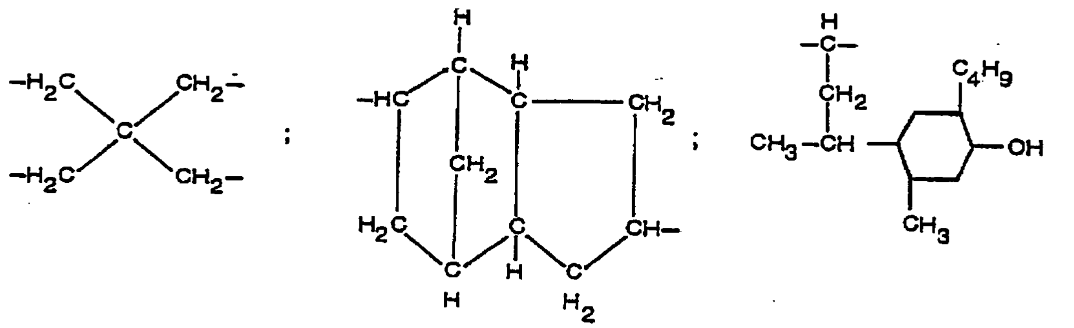
Exemplary Y groups are alkylene, alkylidene, and alkenylene arylene, alkylarylene, arylalkylene, cycloalkylene, cycloalkylidene, and oxa- and thia-substituted such groups; carbonyl groups, tetrahydrofurans, esters and triazino groups. The Y groups are usually bi, tri, or tetravalent, connecting two, three or four Ar groups. However, higher valency Y groups, connecting more than four Ar groups can also be used. According to their constitution, the Y groups can be assigned to subgenera as follows:

(1) Y groups where at least one carbon in a chain or cyclic arrangement connect the aromatic groups, such as:



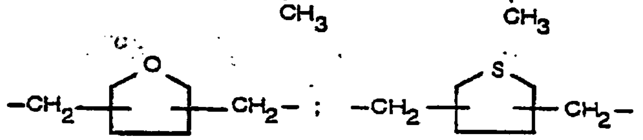


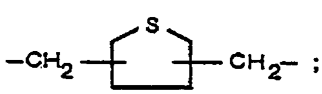




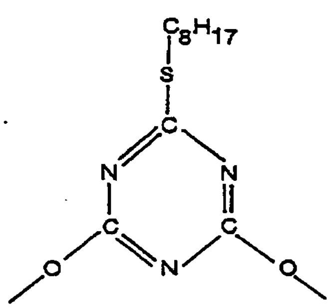
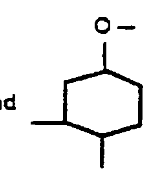
(2) Y groups made up of more than a single atom including both carbon and other atoms linking the aromatic nuclei, such as:

$-CH_2-O-CH_2-$; $-CH(CH_3)-CH_2-O-CH_2-CH(CH_3)-$; $-O-CH_2-CH_2-O-$;

 ; $-S-CH_2-S-$;

 ; $-C(=O)-O-(CH_2)_4-O-C(=O)-$; $C[-CH_2OOCCH_2CH_2-]_4\equiv$;

$-CH_2CH_2-C(=O)-O-CH_2CH_2-O-C(=O)-CH_2CH_2-$;

 ; $-CH_2-S-$; $-CH_2-S-CH_2-$; and  .

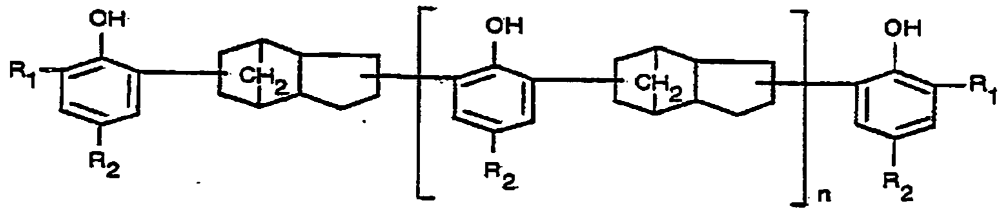
Although the relation of effectiveness to chemical structure is insufficiently understood, many of the most effective phenols have Y groups of subgenus (1), and accordingly this is preferred. Some of these phenols can be prepared by the alkylation of phenols or alkyl phenols with polyunsaturated hydrocarbons such as dicyclopentadiene or butadiene.

Representative phenols include guaiacol, resorcinol monoacetate, vanillin, butyl salicylate, 2,6 - di - tert - butyl - 4 - methyl phenol, 2,6 - di - t - butyl - 4 - sec - butylphenol, 2 - t - butyl - 4 -methoxy phenol, 2,4 - dinonyl phenol, 2,3,4,5 - tetradecyl phenol, tetrahydro - α - naphthol, o-, m- and p-cresol, o-, m- and p-phenylphenol, o-, m- and p-xylenols, the carvenols, symmetrical xylenol, thymol, o-, m- and p-nonylphenol, o-, m- and p-dodecyl-phenol, and o-, m- and p-octyl phenol, o-, and m-tert-butyl - p - hydroxy - anisole, p - n - decyloxy - phenol, p - n - decyloxy - cresol, nonyl - n - decyloxy - cresol, eugenol, isoeugenol, glyceryl monosalicylate, methyl - p - hydroxy - cinnamate, 4 - benzyloxy - phenol, p - acetylaminophenol, p - stearyl - aminophenol, methyl - p - hydroxy benzoate, p - di - chlorobenzoyl - aminophenol, p - hydroxysalicyl anilide, stearyl - (3,5 - dimethyl - 4 - hydroxy - benzyl)thioglycolate, stearyl - β - (4 - hydroxy - 3,5 - di - t - butylphenyl)propionate, distearyl - 3,5 - di - t - butyl - 4 - hydroxybenzylphosphonate, and distearyl(4 - hydroxy - 3 - methyl - 5 - t - butyl)benzylmalonate.

Exemplary polyhydric phenols are orcinol, propyl gallate, catechol, resorcinol, 4 - octyl - resorcinol, 4 - dodecyl - resorcinol, 4 - octadecyl - catechol, 4 - isooctyl - phloroglucinol, pyrogallol, hexahydroxybenzene, 4 - isohexylcatechol, 2,6 - di - tertiary - butylresorcinol, 2,6 - di - isopropyl - phloroglucinol.

Exemplary polyhydric polycyclic phenols are 2,2′ - methylene bis (2,6 - di - tertiary - butyl - phenol), 2,2′ - methylenebis (4 - methyl - 6 - t - butylphenol), 2,2′ - ethylidenebis(4,6 - di - t - butylphenol), 2,2 - bis - (4 - hydroxy phenyl) - propane, methylene bis (p - cresol), 4,4′ - benzylidene bis(2 - tertiary - butyl - 5 - methyl - phenol), 4,4′ - cyclohexylidene bis(2 - tertiary - butylphenol), 2,2′ - methylene bis(4 - methyl - 6 - (1′ - methyl - cyclohexyl)phenol), 2,6 - bis(2′ - hydroxy - 3′ - tertiary - butyl - 5′ - methylbenzyl) - 4 - methylphenol, 4,4′ - bis(2 - tertiary - butyl - 5 - methylphenol), 2,2′ - bis(4 - hydroxy - phenyl)butane, ethylene bis(p - cresol), 2,2′ - methylenebis (4 - methyl - 6 - nonylphenol), 4,4′ - isopropylidenebis (2,6 - di - t - butylphenol), 4,4′ - butylidene bis (2,6 - di - t - butylphenol), 4,4′ - butylidenebis(6 - t - butyl - m - cresol), 1,1,3 - tris(2 - methyl - 4 - hydroxy - 5 - t - butylphenyl)butane, 2,6 - bis (2 - hydroxy - 3 - nonyl - 5 - methylbenzyl) - 4 - methylphenol, 4,4′ - n - butylidene - (2 - t - butyl - 5 - methylphenol), 2,2′ - methylenebis(4 - methyl - 6 - (1′ - methyl - cyclohexyl)phenol), 4,4′ - cyclohexylenebis (2 - tertiary - butylphenol), 2,6 - bis(2′ - hydroxy - 3′ - t - butyl - 5′ - methylbenzyl) - 4 - methylphenol, 1,3′ - bis(naphthalene - 2,5 - diol)propane, and 2,2′ - butylenebis(naphthalene - 2,7 - diol), (3 - methyl - 5 - tert - butyl - 4 - hydroxyphenyl) - 4′ - hydroxyphenyl)propane, 2,2′ - methylenebis (4 - methyl - 5 - isopropylphenol), 2,2′ - methylenebis(5 - tert - butyl - 4 - chlorophenol), (3,5 - di - tert - butyl - 4 - hydroxyphenyl) - (4′ - hydroxyphenyl)ethane, (2 - hydroxyphenyl) - (3′,5′ - di - tert - butyl - 4′,4 - hydroxyphenyl)ethane, 2,2′ - methylenebis(4 - octylphenol), 4,4′ - propylenebis(2 - tert - butyl - phenol), 2,2′ - isobutylenebis(4 - nonylphenol), 2,4 - bis(4 - hydroxy - 3 - t - butylphenoxy) - 6 - (n - octylthio) - 1,3,5 - triazine, 2,4,6 - tris(4 - hydroxy - 3 - t - butylphenoxy) - 1,3,5 - triazine, 4,4′ - bis (4 - hydroxyphenyl)pentanoic acid octadecyl ester, cyclopentylene - 4,4′ - bisphenol, 2 - ethylbutylene - 4,4′ - bisphenol, 4,4′ - cyclooctylenebis(2 - cyclohexylphenol), β,β - thiodiethanolbis (3 - tert - butyl - 4 - hydroxy - phenoxy acetate), 1,4 - butanedioIbis(3 - tert - butyl - 4 - hydroxy phenoxy acetate), pentaerythritoltetra - (4 - hydroxyphenol propionate), 2,4,4′ - tri - hydroxy benzophenone, 4,4′ - bis(4 - hydroxyphenol) pentanoic acid octadecyl thiopropionate ester, 1,1,3 - tris - (2′ - methyl - 4′ - hydroxy - 5′ - tert - butylphenyl)butane, 1,1,3 - tris - (1 - methyl - 3 - hydroxy - 4 - tert - butylphenyl)butane, 1,8 - bis - (2 - hydroxy - 5 - methylbenzoyl - n - octane, 1 - methyl - 3 - (3 - methyl - 5 - tert - butyl - 4 - hydroxy - benzyl) - naphthalene, 2,2′ - (2 - butene) - bis - (4 - methoxy - 6 - tert - butyl phenol) - bis - [3,3 - bis - (4 - hydroxy - 3 - t - butylphenyl)butyric acid] glycol ester, 4,4′ - butylidene - bis - (6 - t - butyl - m - cresol), 1,1,3 - tris-(2 - methyl - 4 - hydroxy - 5 - t - butylphenyl)butane, 1,3,5 - tris - (3,5 - di - t - butyl - 4 - hydroxybenzyl) - 2,4,6 - trimethylbenzene, tetrakis [methylene - 3 - (3,5 - di - t - butyl - 4 - hydroxyphenyl)propionate] methane, 1,3,5 - tris - (3,5 - di - t - butyl - 4-hydroxybenzyl)isocyanurate, 1,3,5 - tris - (3,5 - di - t - butyl - 4 - hydroxyphenyl)propionyl - oxyethyl isocyanurate, 2 - octylthio - 4,6 - di - (4 - hydroxy - 3,5 - di - t - butyl)phenoxy - 1,3,5 - triazine, and pentaerythritol hydroxyphenyl propionate, thiodiglycolbis(3,5 - di - t - butyl - 4-hydroxyphenyl propionate), stearyl - 3 - (3,5 - di - t - butyl - 4 - hydroxyphenyl)propionate, bis(4 - t - butyl - 3 - hydroxy - 2,6 - dimethylbenzylthiol)terephthalate, distearyl(4 - hydroxy - 3 - methyl - 5 - t - butyl)benzylmalonate, stearyl (3,5 - dimethyl - 4 - hydroxybenzyl)thioglycolate, bis[3,3 - bis(4 - hydroxy - 3 - t - butylphenyl)butyric acid]glycolester, 4,4′ - thiobis (6 - t - butyl - m - cresol), 1,3,5 - tris(2,6 - dimethyl - 3 - hydroxy - 4 - t - butylbenzyl)isocyanurate and 1,3,5 - tris(2 - hydroxyethyl)isocyanurate - tris(3,5 - di - t - butyl - (4) - hydroxyphenylpropionate).

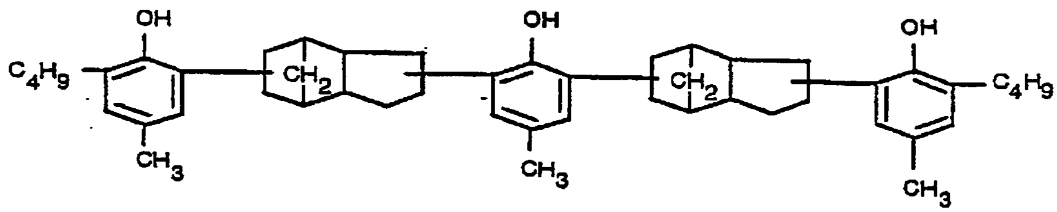
A particularly desirable class of polyhydric polycyclic phenols are the dicyclopentadiene polyphenols, which are of the type:



in which

R_1 and R_2 are lower alkyl, and can be the same or different, and

n is the number of the groups enclosed by the brackets, and is usually from 1 to 5. These are described in US—PS 3,567,683. A commercially available member of this class is Wingstay L®, exemplified by dicyclopentadiene tri-(2-tert-butyl-4-methyl-phenol) of the formula:



The polyhydric polycyclic phenols used in the invention can also be condensation products of phenol or alkylphenols with hydrocarbons having a bicyclic ring structure and a double bond or two or more double bonds, such as α-pinene, β-pinene, dipentene, limonene, vinylcyclohexene, dicyclopentadiene, allo-ocimene, isoprene and butadiene. These condensation products are usually obtained under acidic conditions in the form of more or less complex mixtures of monomeric and polymeric compounds. However, it is usually not necessary to isolate the individual constituents. The entire reaction product, merely freed from the acidic condensation catalyst and unchanged starting material, can be used with excellent results. While the exact structure of these phenolic condensation products is uncertain, the Y groups linking the phenolic nuclei all fall into the preferred subgenus (1). For method of preparation, see e.g., US—PS 3,124,555, 3,242,135 and GB—PS 961,504.

The phosphites and stabilizer compositions of the invention are especially effective in enhancing the resistance to deterioration by heat and light of polyvinyl chloride resins. The term "polyvinyl chloride" as used herein is inclusive of any polymer formed at least in part of the recurring group:

$$\left[\begin{array}{cc} & X \\ & | \\ -CH- & -C- \\ | & | \\ Cl & X \end{array} \right]_n$$

and having chlorine content in excess of 40%. In this group, the X groups can each be either hydrogen or chlorine, and n is the number of such units in the polymer chain. In polyvinyl chloride homopolymers, each of the X groups is hydrogen. Thus, the term includes not only polyvinyl chloride homopolymers but also after-chlorinated polyvinyl chlorides as a class, for example, those disclosed in GB—PS 893,288 and also copolymers of vinyl chloride in a major proportion and other copolymerizable monomers in a minor proportion, such as copolymers of vinyl chloride and vinyl acetate, copolymers of vinyl chloride with maleic or fumaric acids or esters, and copolymers of vinyl chloride with styrene. The stabilizer compositions are effective also with mixtures of polyvinyl chloride in a major proportion with a minor proportion of other synthetic resins such as chlorinated polyethylene or a copolymer of acrylonitrile, butadiene and styrene.

The phosphites and stabilizer compositions are applicable to the stabilization of rigid polyvinyl chloride resin compositions, that is, resin compositions which are formulated to withstand high processing temperatures, of the order of 191°C and higher, as well as plasticized polyvinyl chloride resin compositions of conventional formulation, even though resistance to heat distortion is not a requisite. Conventional plasticizers well known to those skilled in the art can be employed, such as, for example, dioctyl phthalate, octyl diphenyl phosphate and epoxidized soybean oil.

Particularly useful plasticizers are the epoxy higher esters having from 20 to 150 carbon atoms. Such esters will initially have had unsaturation in the alcohol or acid portion of the molecule, which is taken up by the formation of the epoxy group.

Typical unsaturated acids are acrylic, oleic, linoleic, linolenic, erucic, ricinoleic, and brassidic acids, and these may be esterified with organic monohydric or polyhydric alcohols, the total number of carbon atoms of the acid and the alcohol being within the range stated. Typical monohydric alcohols include butyl alcohol, 2-ethyl hexyl alcohol, lauryl alcohol, isooctyl alcohol, stearyl alcohol, and oleyl alcohol. The octyl alcohols are preferred. Typical polyhydric alcohols include pentaerythritol, glycerol, ethylene glycol, 1,2-propylene glycol, 1,4-butylene glycol, neopentyl glycol, ricinoleyl alcohol, erythritol, mannitol and sorbitol. Glycerol is preferred. These alcohols may be fully or partially esterified with the epoxidized acid. Also useful are the epoxidized mixtures of higher fatty acid esters found in naturally-occurring oils such as epoxidized soybean oil, epoxidized olive oil, epoxidized coconut oil, epoxidized cotton-seed oil, epoxidized tall oil fatty acid esters and epoxidized tallow. Of these, epoxidized soybean oil is preferred.

The alcohol can contain the epoxy group and have a long or short chain, and the acid can have a short or long chain, such as epoxystearyl acetate, epoxystearyl stearate, glycidyl stearate, and polymerized glycidyl methacrylate.

The polyvinyl chloride resin can be in any physical form, including, for example, powders, films, sheets, molded articles, foams, filaments and yarns.

A sufficient amount of the phosphite and stabilizer composition is used to enhance the resistance of the polyvinyl chloride to deterioration in physical properties, including, for example, discoloration and embrittlement, under the heat and/or light conditions to which the polymer will be subjected. Very small amounts are usually adequate. Amounts within the range from 0.01 to 5% of the phosphite and from 0.01 to 10% of the stabilizer composition by weight of the polyvinyl chloride resin are satisfactory. Preferably, an amount within the range from 0.05 to 2% of phosphite, and from 0.1 to 5% of stabilizer composition, is employed for optimum stabilizing effectiveness.

The phosphites and stabilizer compositions of the invention can be employed as the sole stabilizers. They can also be used in combination with other conventional heat and light stabilizers for polyvinyl chloride resins, such as, for example, polyvalent metal salts and alkaline earth metal phenolates, as well as epoxy compounds.

A particularly useful stabilizer system contains the following amounts of ingredients:

(a) phosphite in an amount within the range from 25 to 45 parts by weight;

(b) phenolic antioxidant in an amount within the range from 0.01 to 1 part by weight;

(c) polyvalent metal salt of an aliphatic carboxylic acid or of an alkyl phenol in an amount within the range from 25 to 45 parts by weight;

plus any one or more of the following optional ingredients:

(d) free aliphatic carboxylic acid in an amount within the range from 0.5 to 5 parts by weight;

(e) acid phosphite in an amount within the range from 0.5 to 5 parts by weight.

In addition, any of the conventional polyvinyl chloride resin additives, such as lubricants, emulsifiers, antistatic agents, flame-proofing agents, pigments and fillers, can be employed.

Preferably, the stabilizer system is added to the polyvinyl chloride resin in an amount to provide in the resin from 0.2 to 1% of the phosphite; from 0.1 to 2% of phenolic antioxidant; and from 0 to 1% total of one or more of the additional ingredients, as noted above.

The stabilizer system is incorporated in the polymer in suitable mixing equipment, such as a mill or a Banbury mixer. If the polymer has a melt viscosity which is too high for the desired use, the polymer can be worked until its melt viscosity has been reduced to the desired range before addition of the stabilizer. Mixing is continued until the mixture is substantially uniform. The resulting composition is then removed from the mixing equipment and brought to the size and shape desired for marketing or use.

The stabilized polyvinyl chloride resin can be worked into the desired shape, such as by milling, calendering, extrusion or injection molding, or fiber-forming. In such operations, it will be found to have a considerably improved resistance to discoloration and embrittlement on exposure to heat and light.

The phosphites and stabilizer compositions of the invention are especialy effective heat stabilizers for olefin polymers such as polyethylene, polypropylene, polybutylene, polypentylene, polyisopentylene, and higher polyolefins.

Olefin polymers on exposure to elevated temperatures undergo degradation, resulting in embrittlement and discoloration.

The phosphites and stabilizer compositions can be employed with any olefin polymer, especially from α-olefins having from 2 to 6 carbon atoms, including low-density polyethylene, high density polyethylene, polyethylenes prepared by the Ziegler-Natta process, polypropylenes prepared by the Ziegler Natta process, and by other polymerization methods from propylene, poly(butene-1)-poly(pentene-1)poly(3-methylbutene-1)poly(4-methylpentene-1), polystyrene, and mixtures of polyethylene and polypropylene with other copmpatible polymers, such as mixtures of polyethylene and polypropylene, and copolymers of such olefins, such as copolymers of ethylene, propylene, and butene, with each other and with other copolymerizable monomers. The term "olefin polymer" encompasses both homopolymers and copolymers.

Polypropylene solid polymer can be defined in a manner to differentiate it from other polyolefins as having a density within the range from 0.86 to 0.91, and a melting point about 150°C. The

phosphites of the invention are applicable to all such polypropylenes, as distinguished from polypropylenes in the liquid form or in semi-liquid of gel-like forms, such as are used as greases and waxes.

The phosphites and stabilizer compositions of the invention are applicable to polypropylenes prepared by any of the various procedures, for the molecular weight and tacticity are not factors affecting this stabilizer system. Isotactic polypropylene, available commercially under the trade name PRO—FAX®, and having a softening or hot-working temperature of about 177°C, is an example of a sterically regular polypropylene polymer.

Mixtures of polypropylene with other compatible polymers and copolymers of propylene with copolymerizable monomers not reactive with the phosphites or stabilizer composition can also be stabilized, for example, mixtures of polyethylene and polypropylene, and copolymers of propylene and ethylene stabilizer.

The phosphites and stabilizer compositions are also effective to enhance the resistance to heat degradation of polystyrene; polydienes, such as polybutadiene and polyisoprene; and copolymers of olefins and dienes with other ethylenically and acetylenically unsaturated monomers, such as ethylene-vinyl acetate copolymers, styrene-butadiene copolymers, acrylonitrilestyrene-butadiene copolymers, synthetic rubbers of all types, such as polychloroprene; poyvinylidene chloride; and copolymers of vinyl chloride and vinylidene chloride; vinylidene chloride and vinyl acetate; and other ethylenically unsaturated monomers; polyacetals such as polyoxymethylene and polyoxyethylene; polycarbonates; polyphenylene oxides; mixed polyphenylene oxidepolystyrene-poly carbonate; polyesters such as polyethylene glycol-terephthalic acid ester polymers; polyamides such as poly-epsilon-caprolactam; polyhexamethylene adipamide and polydecamethylene adipamide; polyurethanes; and epoxy resins.

The synthetic polymer can be in any physical form, including (for example) filaments, yarns, films, sheets, molded articles, latex and foam.

A sufficient amount of the stabilizer composition including the phosphite and phenolic antioxidant is used to improve the resistance of the synthetic polymer to deterioration in physical properties, including, for example, discoloration, reduction in melt viscosity and embrittlement, under the conditions to which the polymer will be subjected. Very small amounts are usually ádequate. Amounts within the range from 0.001 to 5% total stabilizers by weight of the polymer are satisfactory. Preferably, from 0.01 to 3% is employed, for optimum stabilization.

The stabilizer compositions of the invention can be employed as the sole stabilizers or in combination with other conventional heat and light stabilizers for the particular olefin polymer.

Thus, for example, there can be employed fatty acid salts of polyvalent metals, and the higher fatty acid esters of thiodipropionic acids, such as, for example, dilauryl thiodipropionate.

With polyamide resin compositions, polyamide stabilizers such as copper salts in combination with iodides and/or other phosphorous compounds and salt of divalent manganese can be used.

With synthetic rubbers and acrylonitrile-butadiene-styrene terpolymers, polyvalent metal salts of higher fatty acids can be used.

In addition, other conventional additives for synthetic polymers, such as plasticizers, lubricants, emulsifiers, antistatic agents, flame-proofing agents, pigments and fillers, can be employed.

The stabilizer composition is incorporated in the polymer in suitable mixing equipment, such as a mill or a Banbury mixer. If the polymer has a melt viscosity which is too high for the desired use, the polymer can be worked until its melt viscosity has been reduced to the desired range before addition of the stabilizers. Mixing is continued until the mixture is substantially uniform. The resulting composition is then removed from the mixing equipment and brought to the size and shape desired for marketing or use.

The satabilized polymer can be worked into the desired shape, such as by milling, calendering, extruding or injection molding or fiber-forming. In such operations, it will be found to have a considerably improved resistance to reduction in melt viscosity during the heating, as well as better resistance to discoloration and embrittlement on ageing and heating.

The following Examples illustrate preferred stabilizer compositions and resin compositions of the invention:

Examples 1 to 3

A group of cis-1,4-polisoprene compositions was prepared, having the following formulation:

Ingredient	Parts by Weight
Poly-cis-1,4-isoprene (Mol. weight 680,000)	100
Pentaerythritol tetrakis (3,5-di-tert-butyl-4-hydroxyphenyl) propionate	0.1
Phosphite shown in Table I	0.2

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The cis-1,4-polyisoprene, pentaerythritol tetrakis (3,5-di-t-butyl-4-hyroxyphenyl propionate) and phosphite were dissolved in 250 ml of isooctane, and the isooctane was then distilled off. This polyisoprene composition was heated at 100°C in a Geer oven for three hours and color of the composition was observed, and the inherent viscosity in toluene solution before and after the heating was measured.

The results are shown in Table I.

TABLE I

Example No.	Phosphite	Color of composition	Inherent viscosity Original	Inherent viscosity After Heating
Control				
1	None	Brown	4.7	—
2	Tris(2,4-di-t-butyl-phenyl) phosphite	Pale Brown	4.6	3.9
3	Bis(2,4-di-t-butyl-phenyl) pentaerythritol diphosphite	Yellow	4.5	3.7
Example				
1	2,6-Di-t-butyl-4-methyl-phenyl phenylpentaerythritol diphosphite	Colorless	4.6	4.4
2	2,6-Di-t-butyl-4-methyl-phenyl isooctylpentaerythritol diphosphite	Colorless	4.7	4.4
3	Bis(2,6-di-t-butyl-4-methylphenyl)pentaerythritol diphosphite	Colorless	4.8	4.5

It is apparent from Controls 1, 2 and 3 that in combination with phenolic antioxidant, the phosphites in accordance with the invention give a considerable improvement in effectiveness as compared to the phosphites in the combinations of the Controls.

Examples 4 to 8

Acrylonitrile-styrene copolymer resin compositions were prepared using stabilizer compositions of the invention and having the following formulation:

Ingredient	Parts by Weight
Acrylonitrile-styrene copolymer	100
1,3,5-Tris(2,6-dimethyl-3-hydroxy-4-t-butyl benzyl) isocyanurate	0.05
Phosphite as shown in Table II	0.05

The stabilizers were blended with the resin on a two-roll mill, and extruded at 230°C. Samples were prepared by injection molding of the resulting blend, and yellowness measured in a Hunter color difference meter.

Samples were heated at 230°C for ten minutes before molding, and yellowness again measured in a Hunter color difference meter. Samples were also heated at 230°C for twenty minutes, and yellowness measured in the same way.

The results are shown in Table II:

TABLE II

Example No.	Phosphite	Yellowness Original	Yellowness After 10 Minutes	Yellowness After 20 Minutes
Control				
1	Bis(2,4-di-t-butyl-5-methylphenyl) pentaerythritol diphosphite.	15	20	33
2	Bis(2,6-di-t-butylphenyl) pentaerythritol diphosphite	18	22	36
Example				
4	Bis(2,6-di-t-butyl-4-methylphenyl) pentaerythritol diphosphite	12	14	18
5	Bis(2,6-di-t-butyl-4-ethylphenyl) pentaerythritol diphosphite	11	13	17
6	2,6-Di-t-butyl-4-methylphenyl cyclohexyl pentaerythritol diphosphite	10	12	15
7	2,6-Di-t-butyl-4-methylphenyl tridecyl pentaerythritol. diphosphite	10	12	15
8	2,6-Di-t-butyl-4-methylphenyl 2-cyclohexylphenyl pentaerythritol diphosphite	12	15	19

It is apparent from the data that the phosphites of the invention are far superior to the phosphites of the Controls.

Examples 9 to 13

Acrylinitrile-butadiene-styrene terpolymer resin compositions were prepared using stabilizer compositions of the invention and having the following formulation:

Ingredient	Parts by Weight
Acrylonitrile-butadiene-styrene terpolymer	100
Calcium stearate	1.0
1,3,5-Tris-(3,5-di-t-butyl-4-hydroxy benzyl) isocyanurate	0.1
Phosphite as shown in Table III	0.3

The stabilizers were blended with the resin on a two-roll mill and extruded at 200°C, followed by injection molding at 230°C of the resulting blend, to prepare samples.

Heat stability was evaluated by heating the specimen samples at 135°C in a Geer oven for thirty hours. The whiteness of the specimens was evaluated using a Hunter color difference meter. Izod impact strength of the specimens was determined before and after immersion in hot water at 100°C for seventy-two hours.

The results are shown in Table III.

TABLE III

Example No.	Phosphite	Whiteness	Izod impact strength (kg.cm/cm) Original	After Heating	After Immersion
Control					
1	Bis(2,4-di-t-butyl-6-methylphenyl)pentaerythritol diphosphite		17.6	13.3	13.5
Example					
9	2,6-Di-t-butyl-4-methylphenyl isooctyl pentaerythritol diphosphite		18.7	17.2	17.6
10	2,6-Di-t-butyl-4-methylphenyl stearyl pentaerythritol diphosphite		19.2	17.5	17.8
11	2,6-Di-t-butyl-4-methylphenyl benzyl pentaerythritol diphosphite		18.0	16.9	16.2
12	Bis(2,6-di-t-butyl-4-methylphenyl) pentaerythritol diphosphite		18.5	17.2	16.7
13	2,6-Di-t-butyl-4-methylphenyl nonylphenyl pentaerythritol diphosphite		18.4	17.0	16.5

It is apparent from the data that in the stabilizer compositions of the invention, the phosphites of the invention are far superior to the Control.

Examples 14 to 19

Polypropylene compositions were prepared using stabilizer compositions of the invention and having the following formulation:

Ingredient	Parts by Weight
Polypropylene (Profax 6501®)	100
Ca stearate	0.2
Dilauryl thiodipropionate	0.2
Pentaerythritol tetrakis (3,5-di-t-butyl-4-hydroxyphenyl) propionate	0.1
Phosphite as shown in Table IV	0.1

The compositions were thoroughly blended for five minutes in a Brabender Plastograph.

One part of the mixture was then extruded at 20 rpm, cylinder temperature 230 to 240°C and head die temperature 250°C. Another part was injection molded at 475 kg/cm^2, cylinder temperature 240°C, nozzle temperature 250°C, to form sheets 95 × 40 × 1 mm.

Pieces 2.5 cm² were cut off from the sheets and heated at 160°C in a Geer oven to evaluate heat stability.

The time in hours required for the sheet to develop a noticeable discoloration and/or embrittlement was noted as the hours to failure.

The yellowness of the sheet after exposure to ultraviolet light for 72 hours was measured in a Hunter color difference meter.

The results obtained are shown in Table IV.

TABLE IV

Example No.	Phosphite	Hours to failure	Yellowness (%) Original	Yellowness (%) After 72 hours
Control	Bis(2,6-di-t-butylphenyl) pentaerythritol diphosphite	538	9.0	11.2
Example				
14	Bis(2,6-di-t-butyl-4-methyl-phenyl pentaerythritol diphosphite	685	7.8	9.1
15	Bis(2,6-di-t-butyl-4-ethyl-phenyl)pentaerythritol diphosphite	638	7.9	9.5
16	2,6-Di-t-butyl-4-methyl-phenyl-3,6-dioxadecyl penta-erythritol diphosphite	653	7.7	9.2
17	2,6-Di-t-butyl-4-methyl-phenyl-3,6,9-trioxatridecyl pen-taerythritol diphosphite	703	7.9	9.5
18	2,6-Di-t-butyl-4-ethyl-phenyl isodecyl penta-erythritol diphosphite	684	7.8	9.4
19	2,6-Di-t-butyl-4-ethyl-phenyl-4-t-butylphenyl pentaerythritol diphosphite	712	7.6	9.3

It is apparent from the above results that in the stabilizer compositions of the invention the phosphites are superior to the Control in enhancing resistance of the polypropylene polymer composition to deterioration when heated and when exposed to ultraviolet light.

Examples 20 to 30

Polypropylene compositions were prepared using stabilizer compositions of the invention with a variety of phenolic antioxidants, and having the following formulation:

Ingredient	Parts by Weight
Polypropylene (Profax 6501®)	100
Ca stearate	0.2
Dilauryl thiodipropionate	0.2
Bis(2,6-di-t-butyl-4-methylphenyl)pentaerythritol diphosphite	0.1
Phenolic antioxidant as show in Table V	0.1

The composition was thoroughly blended for five minutes in a Brabender Plastograph.

One part of the mixture was then extruded at 20 rpm, cylinder temperature 230 to 240°C and head die temperature 250°C. Another part was injection-molded at 466 bar, cylinder temperature 240°C, nozzle temperature 250°C, to form sheets 95 x 40 x 1 mm.

Pieces 2.5 cm^2 were cut off from the sheets and heated at 160°C in a Geer oven to evaluate heat stability.

The time in hours required for the sheets to develop a noticeable discoloration and/or embrittlement was noted as the hours to failure.

The yellowness of the sheet after exposure to ultraviolet light for 72 hours was measured in a Hunter color difference meter.

The results obtained are shown in Table V.

TABLE V

Example No.	Phenolic Antioxidant	Heat Stability (hours)	Yellowness (%) Original	Yellowness (%) After 72 hours
control	None	24	12.3	—
Example				
20	2,6-Di-t-butyl-4-methylphenol	98	10.3	15.2
21	4,4′-Butylidenebis(2-t-butyl-5-methylphenol)	183	9.7	12.7
22	1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl) butane	216	9.8	12.4
23	1,3,5-Trimethyl-2,4,6-tris (3,5-di-t-butyl-4-hydroxybenzyl) benzene	335	9.1	11.6
24	Stearyl-3,5-di-t-butyl-4-hydroxyphenyl propionate	642	7.7	9.3
25	Thiodiethylene glycolbis (3,5-di-t-butyl-4-hydroxy-phenyl)propionate	628	8.2	9.9
26	1,6-Hexanediolbis(3,5-di-t-butyl-4-hydroxyphenyl propionate)	620	7.8	9.6
27	1,3,5-Tris(2-hydroxyethyl isocyanurate tris(3,5-di-t-butyl-4-hydroxyphenyl propionate)	674	8.0	9.2
28	Pentaerythritol tetrakis (3,5-di-t-butyl-4-hydroxyphenyl propionate)	685	7.8	9.1
29	1,3,5-Tris(3,5-di-t-butyl-4-hydroxybenzyl) isocyanurate	716	7.6	9.0
30	1,3,5-Tris(2,6-dimethyl-4-t-butyl-3-hydroxybenzyl) isocyanurate	650	7.8	9.3

It is apparent from the above data that the phenolic antioxidants appreciably improve the effectiveness of the phosphite Control.

Examples 31 to 35

High density polyethylene compositions were prepared using stabilizer compositions of the invention, and having the following formulation:

Ingredient	Parts by Weight
High-density polyethylene (Hizex 5100E®)	100
Distearyl thiodipropionate	0.3
Stearyl 3,5-di-t-butyl-4-hydroxyphenyl propionate	0.1
Phosphite as shown in Table VI	0.1

The stabilizers were blended with the polymer on a two-roll mill at 150°C for five minutes, and sheets 1 mm thick were prepared by compression molding of the blend at 150°C and 180 bar pressure.

Pieces 10 x 20 mm were cut off from the sheets, and heated at 150°C in a Geer oven on aluminium foil.

The time in hours when degradation set in, as determined by a significant discoloration and/or embrittlement, was noted as hours to failure.

The results are reported in Table VI.

TABLE VI

Example No.	Phosphite	Hours to Failure
Control	Bis(2-t-butyl-4,6-dimethylphenyl) pentaerythritol diphosphite	523
Example		
31	Bis(2,6-di-t-butyl-4-methylphenyl) pentaerythritol diphosphite	683
32	2,3-Di-t-butyl-4-methylphenyl isotridecyl pentaerythritol diphosphite	675
33	2,6-Di-t-butyl-4-methylphenyl-2-ethylhexyl pentaerythritol diphosphite	702
34	2,6-Di-t-butyl-4-ethylphenyl dinonylphenyl pentaerythritol diphosphite	648
35	2,6-Di-t-butyl-4-ethylphenyl-4-t-octylphenyl pentaerythritol diphosphite	650

It is apparent from the above results that the phosphites of the invention are superior to the Control phosphite in enhancing the resistance of the polyethylene polymer composition to deterioration when exposed to heat.

Examples 36 to 40

Resin compositions having the following composition were prepared:

Ingredient	Parts by Weight
Poly(2,6-dimethyl-1,4-phenyleneoxide)	50
Polystyrene	47.5
Polycarbonate	2.5
TiO_2	3
Phosphite as shown in Table VII	0.5

The ingredients were mixed and then extruded at 60 rpm, 260°C, followed by injection molding at 290°C to prepare the test pieces. The heat stability was evaluated by heating the test pieces in a Geer oven at 125°C for 100 hours. Elongation and Izod impact strength were measured before and after the heating, and the percent elongation and percent Izod impact strength retaining were calculated.

The results are shown in Table VII.

TABLE VII

Example No.	Phosphite	% Elongation Retained	% Izod Impact Strength Retained
Control	Bis(2,4-di-t-butyl-6-methylphenyl) pentaerythritol diphosphite	40	53
Example			
36	Bis(2,6-di-t-butyl-4-methylphenyl) pentaerythritol diphosphite	58	71
37	2,6-Di-t-butyl-4-methylphenyl-2,4-di-t-butylphenyl pentaerythritol diphosphite	52	69
38	2,6-Di-t-butyl-4-methylphenyl lauryl pentaerythritol diphosphite	54	75
39	2,6-Di-t-butyl-4-ethylphenyl-2-phenylphenyl pentaerythritol diphosphite	50	68
40	2,6-Di-t-butyl-4-ethylphenyl oleyl pentaerythritol diphosphite	54	70

The phosphites of the invention are clearly more effective heat stabilizers than the Control phosphite.

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Examples 41 to 43

Polycarbonate resin compositions were prepared having the following formulation:

Ingredient	Parts by Weight
Polycarbonate	100
Phosphite as shown in Table VIII	0.2

The ingredients were mixed and compression-molded at 260°C to prepare a sheet 1 mm thick. Heat stability was evaluated by heating the sheets in a Geer oven at 230°C for thirty minutes, and then observing the color of the sheets.

The results are shown in Table VII

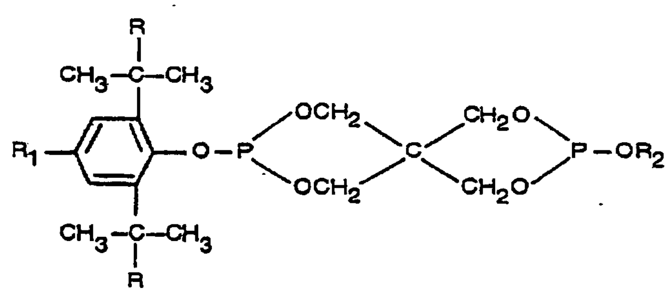
TABLE VIII

Example No.	Phosphite	Color of Sheet
Control	Bis(2,4-di-t-butylphenyl) pentaerythritol diphosphite	Yellow
Example		
41	Bis(2,6-di-t-butyl-4-methylphenyl) pentaerythritol diphosphite	Colorless
42	Bis(2,6-di-t-butyl-4-ethylphenyl) pentaerythritol diphosphite	Colorless
43	2,6-Di-t-butyl-4-methylphenyl isodecyl pentaerythritol diphosphite	Colorless

The phosphites of the invention are clearly more effective heat stabilizers than the Control phosphite.

Claims

1. 2,6-Di-tertiary butyl phenyl pentaerythritol spiro bis-phosphites having the structure:



wherein:

R is alkyl having from 1 to 6 carbon atoms;

R_1 is methyl or ethyl; and

R_2 is selected from alkyl having from 1 to 8 carbon atoms; cycloalkyl having from 3 to 12 carbon atoms; and alkaryl and aryl having from 6 to 30 carbon atoms; such groups substituted with from 1 to 4 oxy ether (—O—) and/or carboxylic ester (—COO—) groups;

the residue of a polyhydric alcohol having from 2 to 18 carbon atoms, and 2 to 10 hydroxyl groups, the residue R_2 being bond to the phosphorus atom by an oxy group of a hydroxyl group; and the residue of a polyphenol having from 6 to 18 carbon atoms and from 2 to 10 phenolic hydroxyl groups, the residue R_2 being bond to the phosphorus atom by an oxy group of a phenolic group and R_2 may be a benzyl radical when R is a methyl radical and R_1 is an ethyl radical.

2. 2,6-Di-tertiary butyl phenyl pentaerythritol spiro bis-phosphites according to claim 1 in which the R is methyl or ethyl and/or R_1 is methyl.

3. 2,6-Di-tertiary butyl phenyl pentaerythritol spiro bis-phosphites according to claim 1 or 2 in which R_2 is alkyl or alkyl substituted with oxyethyl (—O—).

4. 2,6-Di-tertiary butyl phenyl pentaerylthritol spiro bisphosphites according to claim 1 to 3 in which R_2 is alkyl substituted with carboxylic ester (COO—), cycloalkyl, aryl, alkaryl, the residue of a polyhydric alcohol or the residue of a polyphenol.

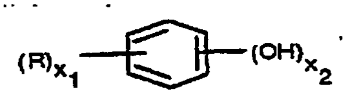
5. 2,6-Di-tertiary butyl phenyl pentaerythritol spiro bis-phosphites according to claim 1 in which R and R_1 are each methyl and R_2 is alkyl, the residue of a polyhydric alcohol or the residue of a polyphenol.

6. A compound according to claim 1, namely 2,6-di-t-butyl-4-methylphenyl-isotridecyl pentaerythritol diphosphite, 2,6-di-t-butyl-4-ethylphenyl-2-ethylhexyl pentaerythritol diphosphite, 2,6-di-t-butyl-4-methylphenyl-2-cyclohexylphenyl pentaerythritol diphosphite.

7. A compound according to claim 1, namely bis (2,6-di-t-butyl-4-methylphenyl)-pentaerythritol diphosphite and bis(2,6-di-t-butyl-4-ethylphenyl) pentaerythritol diphosphite.

8. A stabilizer composition capable of enhancing resistance to deterioration by heat and/or light of synthetic resin compositions comprising a phenolic antioxidant and a phosphite according to claim 1.

9. A stabilizer composition according to claim 8 in which the phenolic antioxidant has the formula:



wherein:

R is selected from the group consisting of hydrogen; halogen; and organic radicals containing from 1 to 30 carbon atoms; and

x_1 and x_2 are integers from one to four, and the sum of x_1 and x_2 does not exceed six.

10. A stabilizer composition according to claim 9 in which the phenolic antioxidant has the formula:

$$\begin{array}{ccc} (Ar)_{n_1} & —Y— & (Ar)_{n_2} \\ | & & | \\ (OH)_{m_1} & & (OH)_{m_2} \end{array}$$

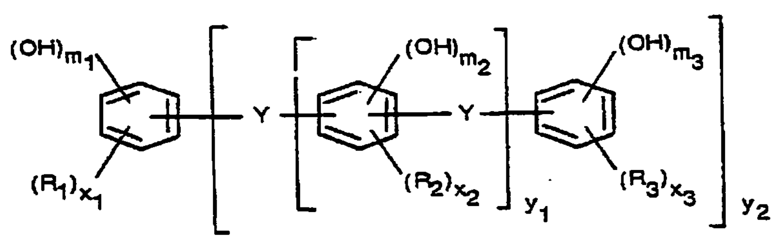
wherein:

Y is a polyvalent linking groiup selected from the group consisting of oxygen; carbonyl; sulfur; sulfinyl; and aromatic, aliphatic and cycloaliphatic hydrocarbon groups and oxyhydrocarbon, thiohydrocarbon and heterocyclic groups having from 1 to 20 carbon atoms;

Ar is a phenolic nucleus having at least one up to five free phenolic hydroxyl groups; and

m_1 and m_2 are numbers from one to five, and n_1 and n_2 are numbers from one to four.

11. A stabilizer composition according to claim 9 in which the phenolic antioxidant has the formula:



wherein:

R_1, R_2 and R_3 are inert substituent groups selected from halogen, alkyl, aryl, alkaryl, aralkyl, cycloalkenyl, cycloalkyl, alkoxy, aryloxy and acyloxy

$$(R'\underset{\underset{O}{\|}}{C}—O)$$

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where R′ is aryl, alkyl or cycloalkyl containing from 1 to 30 carbon atoms; thiohydrocarbon groups having from 1 to 30 carbon atoms, and carboxyl groups;

m_1 and m_3 are integers from one to a maximum of five;

m_2 is an integer from one to a maximum of four;

x_1 and x_3 are integers from zero to four; and

x_2 is an integer from zero to three;

y_1 is an integer from zero to six; and

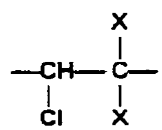
y_2 is an integer from one to five.

12. A stabilizer composition according to claim 9 in which the phenolic antioxidant is pentaerythritol tetrakis 1,3,5-tris(2,6-dimethyl-3-hydroxy-4-t-butylbenzyl)isocyanurate, 1,3,5-tris(3,5-di-t-butyl-4-hydroxybenzyl)isocyanurate, 1,3,5-tris(2-hydroxyethyl) isocyanurate-tris(3,5-di-t-butyl-hydroxyphenyl propionate).

13. A stabilizer composition according to claim 9 in which the phenolic antioxidant is pentaerythritol tetrakis (3,5-t-butyl-4-hydroxyphenyl propionate) or stearyl-3,5-di-t-butyl-4-hydroxyphenyl propionate.

14. Synthetic resin composition with improved resistance to deterioration containing a phosphite according to any of the claims 1 to 7.

15. Composition according to claim 14 comprising a polyvinyl chloride resin formed at least in part of the recurring group

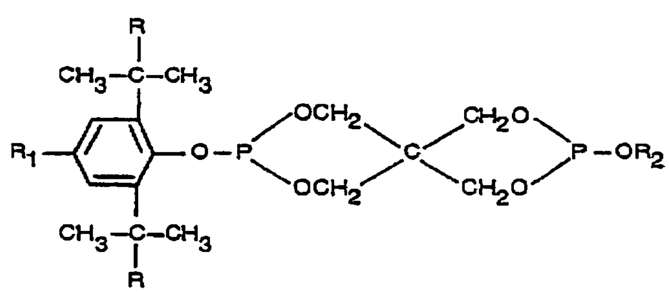


and having a chlorine content in excess of 40%, where X is either hydrogen or chlorine, preferably polyvinyl chloride homopolymer or a copolymer of vinyl chloride and vinyl acetate, and a phosphite in accordance with any of the claims 1 to 7 or a stabilizer composition according to any of the claims 8 to 13, having improved resistance to deterioration when heated at 177°C.

16. Composition according to claim 14 comprising an olefin polymer selected from the group consisting of polymers of alpha-olefins having from two to six carbon atoms and polystyrene, preferably polypropylene, polyethylene or cis-1,4-polyisoprene, an acrylonitrile-butadiene-styrene terpolymer or acrylonitrile-styrene copolymer, a polycarbonate resin or a mixed polyphenylene-oxide-polystyrene-polycarbonate polymer, and a phosphite according to any of the claims 1 to 7 or a stabilizer composition according to any of the claims 8 to 13.

Revendications

1. Bis-phosphites de 2,6-di-t-butylphényl-spiro-pentaérythritol, ayant la structure:



dans laquelle

R est un groupe alkyle ayant de 1 à 6 atomes de carbone;

R_1 est un groupe méthyle ou éthyle;

R_2 est choisi parmi un groupe alkyle ayant de 1 à 18 atomes de carbone; cycloalkyl ayant de 3 à 12 atomes de carbone; et alcaryle et aryle ayant de 6 à 30 atomes de carbone, de tels groupes substitués par 1 à 4 groupes oxyéther (—O—) et/ou ester carboxylique (—COO—); le radical d'un polyalcool comportant de 2 à 18 atomes de carbone et de 2 à 10 groupes hydroxyles, le radical R_2 étant relié à l'atome de phosphore par un groupe oxy d'un groupe hydroxyle; et le radical d'un polyphénol ayant de 6 à 18 atomes de carbone et de 2 à 10 groupes hydroxyles phénoliques, le radical R_2 étant relié à l'atome de phosphore par un groupe oxy d'un groupe phénolique, et R_2 peut être un radical

benzyle lorsque R est un radical méthyle et que R_1 est un radical éthyle.

2. Bis-phosphites de 2,6-di-t-butyl-phényl-spiro-pentaérythritol selon la revendication 1, dans lesquels le radical R est un groupe méthyle ou éthyle et/ou R_1 est un groupe méthyle.

3. Bis-phosphites de 2,6-di-t-butyl-phényl-spiro-pentaérythritol selon la revendication 1 ou 2, dans lesquels R_2 est un radical alkyle ou alkyle substitué par de l'oxyéther (—O—).

4. Bis-phosphites de 2,6-di-t-butylphényl-spiro-pentaérythritol selon la revendication 1 à 3, dans lesquels R_2 est un radical alkyle substitué par un groupe ester carboxylique (COO—), cycloalkyle, aryle, alcaryle, le radical d'un polyalcool ou le radical d'un polyphénol.

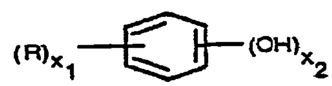
5. Bis-phosphites de 2,6-di-t-butylphényl-spiro-pentaérythritol selon la revendication 1, dans lesquels R et R_1 représentent chacun un radical méthyle, et R_2 est un radical alkyle, le radical d'un polyalcool ou le radical d'un polyphénol.

6. Composé selon la revendication 1, à savoir le diphosphite de 2,6-di-t-butyl-4-méthylphényl-isotridécyl-pentaérythritol, le diphosphite de 2,6-di-t-butyl-4-éthylphényl-2-éthylhexyl-pentaérythritol, le diphosphite de 2,6-di-t-butyl-4-méthylphényl-2-cyclohexylphényl-pentaérythritol.

7. Composé selon la revendication 1, à savoir le diphosphite de bis(2,6-di-t-butyl-4-méthyl-phényl)-pentaérythritol et le diphosphite de bis(2,6-di-t-butyl-4-éthylphényl)-pentaérythritol.

8. Composition stabilisante capable d'amplifier la résistance à une détérioration, par de la chaleur et/ou de la lumière, de compositions de résine synthétique, comprenant un antioxygène phénolique et un phosphite selon la revendication 1.

9. Composition stabilisante selon la revendication 8, dans laquelle l'antioxygène phénolique possède la formule



dans laquelle:

R est choisi dans l'ensemble constitué par un atome d'hydrogène; un atome d'halogène; et des radicaux organiques contenant de 1 à 30 atomes de carbone; et

x_1 et x_2 sont des nombres entiers valant 1 à 4, et la somme de x_1 et x_2 n'excède pas 6.

10. Composition stabilisante selon la revendication 9, dans laquelle l'antioxygène phénolique a pour formule:

$$\underset{|\atop (OH)_{m_1}}{(Ar)_{n_1}} — Y — \underset{|\atop (OH)_{m_2}}{(Ar)_{n_2}}$$

dans laquelle

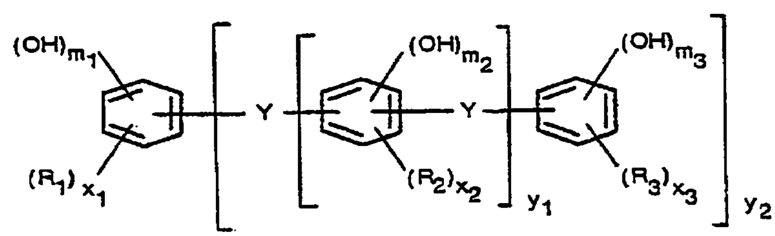
Y est un groupe polyvalent de liaison choisi dans l'ensemble constitué par un atome d'oxygène; un groupe carbonyle, un atome de soufre; un groupe sulfinyle; et des groupes hydrocarbonés, aromatiques, aliphatiques et cycloaliphatiques et des groupes oxyhydrocarbonés, thiohydrocarbonés et hétérocycliques ayant de 1 à 20 atomes de carbone;

Ar est un noyau phénolique comportant au moins 1 jusqu'à 5 groupes hydroxyles phénoliques libres; et

m_1 et m_2 sont des nombres valant 1 à 5, et

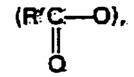
n_1 et n_2 sont des nombres valant 1 à 4.

11. Composition stabilisante selon la revendication 9, dans laquelle l'antioxygène phénolique a pour formule:



dans laquelle

R_1, R_2 et R_3 sont des substituants inertes choisis parmi un atome d'halogène; un groupe alkyle, aryle, alkaryle, aralkyle, cycloalcényle, cycloalkyle, alcoxy, aryloxy et acyloxy



formule

dans laquelle

R' est un groupe aryle, alkyle ou cycloalkyle contenant de 1 à 30 atomes de carbone; un groupe thiohydrocarboné comportant de 1 à 30 atomes de carbone et un groupe carboxyle;

m_1 et m_2 sont des nombres entiers valant de 1 à un maximum de 5;

m_1 est un nombre entier valant de 1 à un maximum de 4;

x_1 et x_3 sont des nombres entiers valant de 0 à 4;

x_2 est un nombre entier valant de 0 à 3;

y_1 est un nombre entier valant de 0 à 6; et

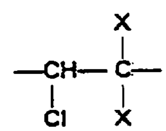
y_2 est un nombre entier valant de 1 à 5.

12. Composition stabilisante selon la revendication 9, dans laquelle l'antioxygène phénolique est du tétrakis-[1,3,5-tris(2,6-diméthyl-3-hydroxy-4-t-butylbenzyl)isocyanurate] de pentaérythritol, de l'isocyanurate de 1,3,5-tris(3,5-di-t-butyl-4-hydroxybenzyle), de l'isocyanurate de 1,3,5-tris(2-hydroxyéthyl)-tris(propionate de 3,5-di-t-butyl-hydroxyphényle).

13. Composition stabilisante selon la revendication 9, dans laquelle l'antioxygène phénolique est du pentaérythritol tétrakis(propionate de 3,5-t-butyl-4-hydroxyphényle) ou du 3,5-di-t-butyl-4-hydroxyphényl-propionate de stéaryle.

14. Composition de résine synthéthique ayant une meilleure résistance à la détérioration, et contenant un phosphite selon l'une quelconque des revendications 1 à 7.

15. Composition selon la revendication 14, comprenant une résine de poly(chlorure de vinyle) formée au moins en partie du groupe récurrent:

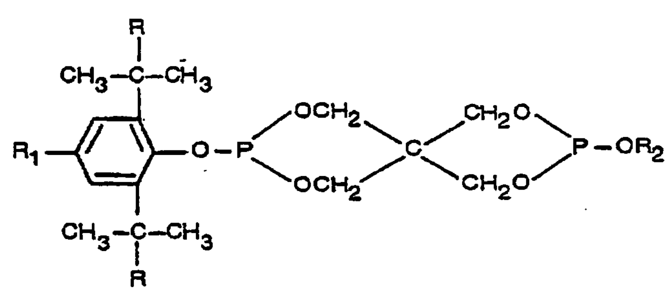


et ayant une teneur en chlore excédant 40%, formule dans laquelle X représente l'hydrogène ou le chlore, de préférence un homopolymère de type poly(chlorure de vinyle) ou un copolymère de chlorure de vinyle ou d'acétate de vinyle, et un phosphite selon l'une quelconque des revendications 1 à 7 ou une composition stabilisante selon l'une quelconque des revendications 8 à 13, ayant une meilleure résistance à la détérioration en cas de chauffage à 177°C.

16. Composition selon la revendication 14, comprenant un polymère d'oléfine choisi dans l'ensemble constitué par des polymères d'α-oléfine ayant de 2 à atomes de carbone et du polystyrène, de préférence du polypropylène, du polyéthylène ou du cis-1,4-polyisoprène, un terpolymère acrylonitrile/butadiène/styrène ou un copolymère acrylonitrile/styrène, une résine de polycarbonate ou un polymère mixte poly(oxyde de phénylène)/polystyrène/polycarbonate, et un phosphite selon l'une quelconque des revendications 1 à 7 ou une composition stabilisante selon l'une quelconque des revendications 8 à 13.

Patentansprüche

1. 2,6-Di-tert.butylphenylpentaerythrit-spiro-bis-phosphite mit der Stuktur:



in welcher

R für Alkyl mit 1 bis 6 Kohlenstoffatomen steht;

R_1 Methyl oder Ethyl ist und

R_2 ausgewählt ist aus Alkyl mit 1 bis 18 Kohlenstoffatomen, Cycloalkyl mit 3 bis 12 Kohlenstoffatomen und Alkaryl und Aryl mit 6 bis 30 Kohlenstoffatomen und derartigen Gruppen, die mit 1 bis 4 Oxyether- (—O—) und/oder Carboxylester- (—COO—) Gruppen substituiert sind, aus einem Rest eines mehrwertigen Alkohols mit 2 bis 18 Kohlenstoffatomen und 2 bis 10 Hydroxylgruppen, wobei der Rest R_2 durch eine Oxygruppe einer Hydroxylgruppe an das Phosphoratom gebunden ist; und dem Rest eines Polyphenols mit 6 bis 18 Kohlenstoffatomen und 2 bis 10 phenolischen Hydroxylgruppen, wobei der Rest R_2 durch eine Oxygruppe einer phenolischen Gruppe an das Phosphoratom gebunden ist; und R_2 ein Benzylrest sein kann, wenn R ein Methylrest ist und R_1 ein Ethylrest ist.

2. 2,6-Di-tert.-butylphenylpentaerythrit-spiro-bis-phosphite gemäß Anspruch 1, in welchen R Methyl oder Ethyl und/oder R_1 Methyl ist.

3. 2,6-Di-tert.-butylphenylpentaerythrit-spiro-bisphosphite gemäß Anspruch 1 oder 2, in welchen R_2 Alkyl oder mit Oxyether (—O—) substituiertes Alkyl ist.

4. 2,6-Di-tert.-butylphenylpentaerythrit-spiro-bis-phosphite gemäß Anspruch 1 bis 3, in welchen R_2 für mit Carboxylester (—COO—) substituiertes Alkyl, Cycloalkyl, Aryl, Alkaryl, den Rest eines mehrwertigen Alkohols oder den Rest eines Polyphenols steht.

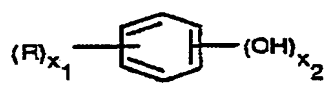
5. 2,6-Di-tert.-butylphenylpentaerythrit-spiro-bis-phosphite gemäß Anspruch 1, in welchen R und R_1 jeweils Methyl sind und R_2 für Alkyl, den Rest eines mehrwertigen Alkohols oder den Ret eines Polyphenols steht.

6. Eine Verbindung nach Anspruch 1, nämlich 2,6-Di-tert.-butyl-4-methylphenyl-isotridecyl-pentaerythrit-diphosphit, 2,6-Di-tert.-butyl-4-ethylphenyl-2-ethylhexyl-pentaerythrit-diphosphit, 2,6-Di-tert.-butyl-4-methylphenyl-2-cyclohexylphenyl-pentaerythrit-diphosphit.

7. Eine Verbindung nach Anspruch 1, nämlich Bis-(2,6-di-tert.-butyl-4-methylphenyl)-pentaerythrit-diphosphit und Bis-(2,6-di-tert.-butyl-4-ethylphenyl)-pentaerythrit-diphosphit.

8. Stabilisatorsusammensetzung, die die Beständigkeit gegen Zersetzung durch Wärme und/oder Licht von synthetischen Harzzusammensetzungen verstärken kann, enthaltend ein phenolisches Antioxidationsmittel und ein Phosphit gemäß Anspruch 1.

9. Stabilisatorzusammensetzung nach Anspruch 8, in welcher das phenolische Antioxidationsmittel die Formel hat:



in welcher

R ausgewählt ist aus der Gruppe, die aus Wasserstoff, Halogen und organischen Resten mit 1 bis 30 Kohlenstoffatomen besteht, und

x_1 und x_2 ganze Zahlen von 1 bis 4 sind, wobei die Summe von x_1 und x_2 6 nicht übersteigt.

10. Stabilisatorzusammensetzung nach Anspruch 9, in welcher das phenolische Antioxidationsmittel die Formel hat:

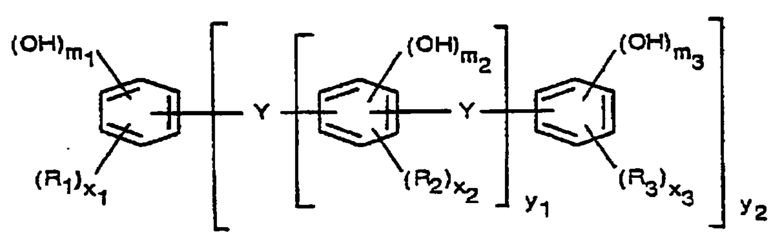
$$\begin{array}{ccc} (Ar)_{n_1} & —Y— & (Ar)_{n_2} \\ | & & | \\ (OH)_{m_1} & & (OH)_{m_2} \end{array}$$

in welcher

Y eine mehrwertige verbindende Gruppe ist, ausgewählt aus der Gruppe, die aus Sauerstoff, Carbonyl, Schwefel, Sulfinyl und aromatischen, aliphatischen und cycloaliphatischen Kohlenwasserstoffgruppen sowie Oxykohlenwasserstoff-, Thiokohlenwasserstoff- und heterocyclischen Gruppen mit 1 bis 20 Kohlenstoffatoman besteht,

Ar ein Phenolkern mit mindestens einer bis zu 5 freien phenolischen Hydroxylgruppen ist, und m_1 und m_2 Zahlen von 1 bis 5 sind und n_1 und n_2 Zahlen von 1 bis 4 sind.

11. Stabilisatorzusammensetzung nach Anspruch 9, in welcher das phenolische Antioxidationsmittel die Formel hat:



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in welcher
R_1, R_2 und R_3 inerte Substituengruppen sind, ausgewählt aus Halogen, Alkyl, Aryl, Alkaryl, Aralkyl, Cycloalkenyl, Cycloalkyl, Alkoxy, Aryloxy und Aryloxy

$$(R'\underset{\underset{\displaystyle O}{\|}}{C}\text{—}O),$$

worin R' Aryl, Alkyl oder Cycloalkyl mit 1 bis 30 Kohlenstoffatomen bedeutet, Thiokohlenwasserstoffgruppen mit 1 bis 30 Kohlenstoffatomen und Carboxylgruppen,
m_1 und m_3 ganze Zahlen von 1 bis maximal 5 sind;
m_2 eine ganze Zahl von 1 bis maximal 4 ist;
x_1 und x_2 ganze Zahlen von 0 bis 4 sind; und
x_2 eine ganze Zahl von 0 bis 3 ist; und
y_1 eine ganze Zahl von 0 bis 6 ist; und
y_2 eine ganze Zahl von 1 bis 5 ist.

12. Stabilisatorzusammensetzung nach Anspruch 9, in welcher das phenolische Antioxidationsmittel Pentaerythrit-tetrakis-1,3,5-tris(2,6-dimethyl-3-hydroxy-4-tert.-butylbenzyl)isocyanuat, 1,3,5-Tris-(3,5-di-tert.-butyl-4-hydroxybenzyl)-isocyanurat, 1,3,5-Tris-(2-hydroxyethyl)-isocyanurat-tris(3,5-di-tert.-butyl-hydroxyphenylpropionat) ist.

13. Stabilisatorzusammensetzung nach Anspruch 9, in welcher das phenolische Antioxidationsmittel Pentaerythrit-tetrakis-(3,5-tert.-butyl-4-hydroxyphenylpropionat) oder Stearyl-3,5-di-tert.-butyl-4-hydroxyphenylpropionat ist.

14. Synthetische Harzzusammensetzung mit verbesserter Beständigkeit gegen Zersetzung, enthaltend ein Phosphit gemäß einem der Ansprüche 1 bis 7.

15. Zusammensetzung nach Anspruch 14, die ein Polyvinylchlorid-Harz, das zumindest teilweise aus der wiederkehrenden Gruppe

$$\text{—}\underset{\displaystyle Cl}{\underset{|}{CH}}\text{—}\underset{\underset{\displaystyle X}{|}}{\overset{\overset{\displaystyle X}{|}}{C}}\text{—}$$

gebildet ist und einen Chlorgehalt von mehr als 40% aufweist, in welcher X entweder Wasserstoff oder Chlor ist, vorzugsweise ein Polyvinylchlorid-Homopolymer oder ein Copolymer von Vinylchlorid und Vinylacetat, und ein Phosphit gemäß einem der Ansprüche 1—7 oder eine Stabilisatorzusammensetzung gemäß einem der Ansprüche 8—13, umfaßt und bei Erhitzung auf 177°C eine verbesserte Widerstandsfähigkeit gegen Zersetzung aufweist.

16. Zusammsetzung nach Anspruch 14, die ein Olefinpolymer ausgewählt aus der Gruppe: Polymere von α-Olefinen mit 2—6 Kohlenstoffatomen und Polystyrol, vorzugsweise Polypropylen, Polyethylen oder cis-1,4-Polyisopren, ein Acrylnitril-Butadien-Styrol-Terpolymer oder Acrylnitril-Styrol-Copolymer, ein Polycarbonat-Harz oder ein gemischtes Polyphenylen-oxid-Polystyrol-Polycarbonat-Polymer, und ein Phosphit nach einem der Ansprüche 1—7 oder eine Stabilisatorzusammensetzung nach einem der Ansprüche 8—13 umfaßt.